Determination of effective diffusion coefficient of water in marshmallow from drying data using finite difference method

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Abstract

The effective diffusion coefficient of water in marshmallow (D_{wm}) was determined by using a combined experimental-computational approach. Marshmallow samples were placed in a desiccator, and sample weights were recorded until there was minimal change (<0.2%, dry basis) over a period of twelve hours. A finite-difference model, accounting for diffusive and convective mass transfer, was developed to simulate the drying experiment. By minimizing the root-mean-square error between the experimental and simulation data, D_{wm} was determined to be $9.49 \times 10^{-11} \pm 0.56 \times 10^{-11}$ m²/s. Results also indicated that the experimental drying process is limited by internal diffusion (Bi > 1).

Introduction

Marshmallow is an aerated confectionary food composed of sugar solution and an aerating agent such as albumen or gelatin (Lees and Jackson, 1973). The ingredients are typically whipped to aerate the mixture (Campbell and Mougeot, 1999); the presence of air adds volume to the mixture and gives marshmallow its foamy characteristic (Lees, 1991). Exact recipes vary widely between manufacturers and the choice of aerating agent, but the dominant component is sugar (Groves, 1995).

Commercial marshmallows have a shelf life between twenty to forty weeks, depending on the temperature and humidity of the storage environment (Tan and Lim, 2008). Marshmallow quality primarily degrades due to hardening, which occurs by a variety of possible mechanisms such as sugar crystallization (Hartel, 1993) and growth or extension of network cross-links (Normand *et al.*, 2000). Sugar crystallization, in particular, is believed to be related to moisture loss (Lees and Jackson, 1973); this is consistent with data showing a hardness increase in marshmallows that have undergone significant moisture loss (Tan and Lim, 2008).

Control of the marshmallow moisture content is also important for maintaining shelf life in some multi-component breakfast cereals. A significant difference between water activities of marshmallows and cereal flakes, for example, would result in overly dry or wet cereal flakes at equilibrium.

Understanding water transport processes in marshmallow would aid in improving control of marshmallow moisture content and product quality. To our knowledge, the diffusion coefficient of water in marshmallow has not been previously reported in literature. This paper describes a combined experimental-computational method used to quantify the diffusion coefficient of water in a commercially-available marshmallow product.

Materials and Methods

Consumer-brand, cylindrical marshmallows (Kraft Jet-Puffed Marshmallows, Northfield, IL) were measured for initial mass, height, and diameter. Each sample was placed on an aluminum-foil tray inside a 225-mm desiccator (Fisher Scientific, 08-615B, Hanover Park, IL) with calcium sulfate (Drierite, Xenia, OH) as the desiccant. Sample mass was recorded until there was less than a ten-milligram change in mass (~0.2%, dry basis) over a period of twelve hours. The final mass, height, and diameter were recorded; the final weight was taken as the dry-basis weight and used to convert weight data to
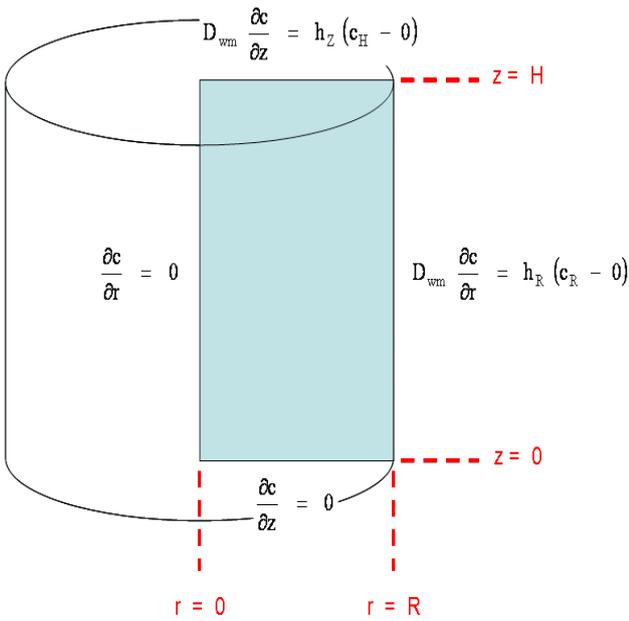
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Figure 1. Schematic for the axisymmetric finite-difference model. The boundary conditions are Neumann flux conditions; no-flux conditions exist at r = 0 and z = 0, and mass conservation is imposed at r = R and z = H

moisture fraction. All experiments were conducted at indoor room temperature (13 – 27°C).

A mathematical model was developed to simulate the drying process. Figure 1 shows the model schematic. Axisymmetry in cylindrical coordinates was employed given the geometry of the marshmallow samples. Water diffusion in the material bulk is described by mass conservation:

$$\frac{\partial c}{\partial t} = D_{wm}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{\partial^2 c}{\partial z^2}\right] \quad (1)$$

where c is moisture fraction (dry basis), t is time, r is radial coordinate, z is axial coordinate, and D_{wm} is effective diffusion coefficient of water in the marshmallow.

Boundary conditions were as follows:

$$\frac{\partial c}{\partial r} = 0 \quad at \quad r = 0 \quad (2)$$

$$\frac{\partial c}{\partial z} = 0 \quad at \quad z = 0 \quad (3)$$

$$D_{wm}\frac{\partial c}{\partial r} = h_R(c_R - 0) \quad at \quad r = R \quad (4)$$

$$D_{wm}\frac{\partial c}{\partial z} = h_Z(c_H - 0) \quad at \quad z = H \quad (5)$$

where R and H are radius and height of the marshmallow sample, respectively, h_R and h_Z are average mass transfer coefficients in those respective directions, and c_R and c_H are moisture fractions at those respective boundaries.

Two of the boundary conditions (equations 2, 3) were zero-mass-flux conditions. The center of the sample (r = 0, equation 2) had no flux due to axisymmetry. The bottom of the sample (z = 0, equation 3) was assumed to have negligible flux since aluminum is relatively impermeable to water.

The remaining two boundary conditions equated the internal rate of diffusion to the external rate of mass transfer. The average mass transfer coefficients were calculated from natural-convection correlations (Mills, 1995):

$$RADIAL: \quad Sh = 0.54\,(Gr\ Sc)^{\frac{1}{4}} \quad (6)$$

$$AXIAL: \quad Sh = 0.68 + 0.67\,(Gr\ Sc\ \Psi)^{\frac{1}{4}} \quad (7a)$$

$$\Psi = \left[1 + \left(\frac{0.492}{Sc}\right)^{\frac{9}{16}}\right]^{-\frac{16}{9}} \quad (7b)$$

where Sh is the Sherwood number $\left(= \frac{hL}{D_{wa}}\right)$, Gr is the Grashof number $\left(= \frac{\Delta c}{c}\frac{gL^3}{v^2}\right)$, Sc is the Schmidt number, L is the $\left(= \frac{v}{D_{wa}}\right)$cteristic length (which is either R or H), D_{wa} is the effective diffusion coefficient of water in air, g is the gravitational constant.

Equation (1) was solved using an in-house program coded in MATLAB (MathWorks, Natick, MA). Spatial discretization was accomplished using finite difference method. The sample was assumed to contain a uniform moisture distribution at start and explicit Euler method (Burden and Faires, 1997) was used for time integration to determine the unsteady moisture concentration. The total moisture content was determined by integrating moisture concentration over the sample volume, and subsequently used to calculate the dry-basis moisture fraction.

The effective diffusion coefficient of water in the sample was numerically determined by minimizing the error between the experimental data and the simulation data. The error was defined as

$$E = \sqrt{\sum_{i=1}^{v}\left[c_{expt}(t_i) - c_{siml}(t_i)\right]^2} \quad (8)$$

where the index i includes all data points between the

Table 1. Geometry and mass of test samples before and after drying experiment. The mass-change p-value is calculated from a paired t-test

N = 8	Initial	Final	Change
Height (cm)	3.02 ± 0.05	3.00 ± 0.05	Not significant
Diameter (cm)	2.95 ± 0.03	2.93 ± 0.04	Not significant
Mass (g)	7.52 ± 0.39	7.01 ± 0.37	0.51 ± 0.03 ($p \sim 10^{-6}$)

initial and final times for the associated experiment.

Results and Discussion

Analytical solutions are available for unsteady mass transfer problems that involve only one spatial dimension or reduce to one spatial dimension by symmetry (Crank, 1980). A computational solution was used because of a lack of analytical solution for equation (1) and boundary conditions (2) through (5). Table 1 shows the initial and final height, diameter, and mass of marshmallow samples before and after drying. The height and diameter did not change significantly, indicating that there was negligible bulk shrinkage. The mass of individual samples ranged from 7.1 to 8.2 g before drying and from 6.6 to 7.6 g after drying. The drying process resulted in approximately the same change in mass (0.51 ± 0.06 g) for all samples. These results indicated that, while there was some variability (~5%) in the geometry and mass of the samples, the initial moisture fraction is relatively constant (6.8 ± 0.6 %).

Figure 2 shows the data for eight drying experiments. The finite-difference model calculated Dwm for each data set, and the results ranged from 7.72×10^{-11} to 10.08×10^{-11} m²/s; the average was $9.49 \times 10^{-11} \pm 0.56 \times 10^{-11}$ m²/s. The model result shown in figure 2 is based on the average D_{wm} value. There was qualitative agreement between experiment and model for all eight runs, though the model clearly overshot the moisture fraction towards the end of the drying process (t > 6 days).

Karathanos *et al.* (1990) conducted forced-convection drying experiments and determined the effective diffusion coefficient of water in gelatinized starches to range from 0.1×10^{-10} to 70×10^{-10} m²/s (40 – 100 °C). Broyart et al. (2007) examined coupled water-salt transport during isothermal drying of pure gelatin gels, and determined the effective diffusion coefficient of water to range from 0.5×10^{-10} to 10.0×10^{-10} m²/s (22 ± 0.6 °C). Ruiz-Cabrera *et al.* (2005) explicitly accounted for spatial effects due to material shrinkage, and reported the effective diffusion coefficient of water in gelatin gels to range from 0.2×10^{-10} to 80×10^{-10} m²/s (24°C). Though
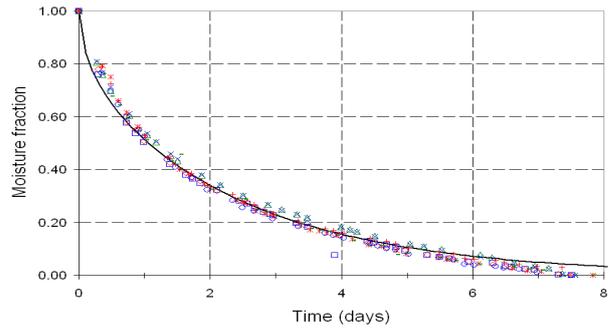

Figure 2. Moisture fraction of marshmallow samples as a function of time. Experimental data for eight drying runs are shown as individual points. Finite-difference model result (solid line) is shown for comparison

our samples were highly specific, the results were consistent with the aforementioned studies.

The mass transfer coefficients h_R and h_Z associated with boundary conditions (4) and (5) were calculated to be 5.39×10^{-4} and 1.31×10^{-3} m/s, respectively.

The associated Biot number $\left(Bi = \dfrac{h\,L}{D_{wm}} \right)$ was on the order of 10^5, indicating that the drying process was limited by internal diffusion. This was verified a posteriori by changing boundary conditions (4) and (5) into Dirichlet conditions that set the external moisture at zero; the results (not shown) were visually identical to Figure 2. Figure 3 shows a representative example of the model-calculated moisture fraction profile. Since h_R was less than h_Z, the moisture fraction gradient near the surface in the radial direction was greater than that in the axial direction.

Natural convection correlations can be notoriously inaccurate for drying experiments. Figure 4 shows how the computed D_{wm} value varied with artificial changes to the external mass transfer. The computed D_{wm} value was relatively insensitive to changes to h_R or h_Z as long as internal diffusion remained the limiting mass transfer resistance (i.e., $Bi > 10^2$).

For gelatinized starch material, the water diffusion coefficient is a function of both porosity and moisture content (Karathanos *et al.*, 1990). A change in porosity and moisture content can occur simultaneously (Senadeera, 2008) as the water leaving food can result in excessive compressive stresses that are unsustainable by the remaining (dry) fiber matrix. Given that the height and diameter of our marshmallow samples did not change significantly, it is unlikely that porosity of the marshmallow samples varied with drying and adversely affected the calculation of D_{wm}. Validation of any change in sample porosity, however, will require anatomical visualization such as microscopy.

The model overshot the moisture fraction towards the end of the drying process (figure 2, t >
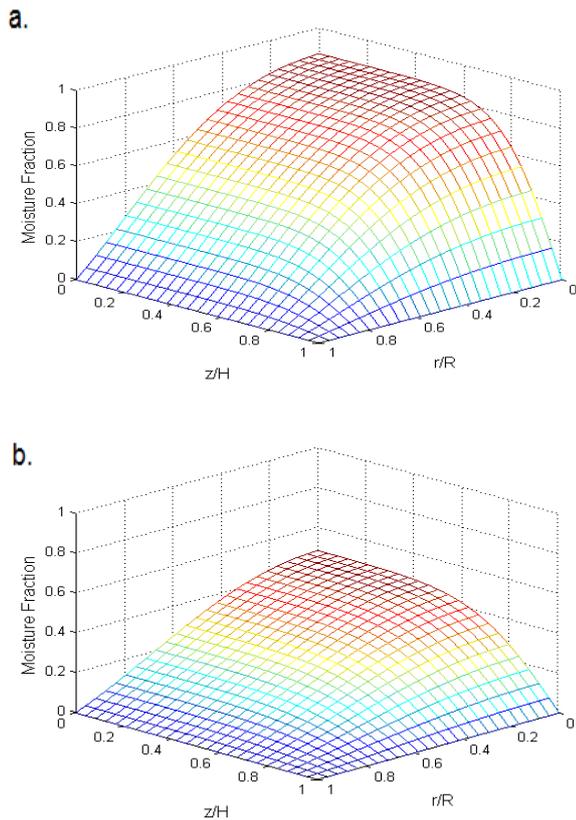
a.

b.

Figure 3. Finite-difference model simulation of the moisture fraction profile at (a) 2 and (b) 4 days. The initial moisture fraction is normalized to one
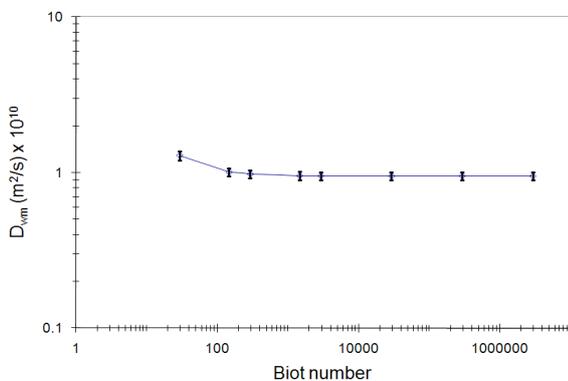

Figure 4. Sensitivity of D_{wm} as a function of an artificially-changed Biot number. Error bars represent one standard deviation (N = 8)

6 days), suggesting that the calculated D_{wm} value underestimated the actual value during the latter stages. One possible explanation on the microscopic scale was suggested by Karathanos *et al.* (1990) after observing an increase in effective water diffusion coefficient with drying: As drying progressed, there was increasingly more air in the space previously occupied by water. Therefore, it became easier for water molecules to transition from liquid diffusion to vapor diffusion within the sample as drying occurred. This explanation was consistent with Bi >> 1, which indicates that drying was limited by water diffusion within the marshmallow sample.

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