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Experimental Analysis and Mathematical Modelling of the Effect of Starch Gelatinization on Chestnuts Rehydration

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The paper presents an experimental and modeling study of the rehydration process of air-dried chestnuts. Sorption curves are obtained for chestnuts dried at 40, 60, and 80 °C immersed in water at 90 °C and differential scanning calorimetry (DSC) measurements are performed to characterize the evolution of the starch gelatinization process on the transport of water during rehydration. In this way, stages of the rehydration process governed by different physical mechanisms are identified. A large growth in the absorption rate is observed at intermediate times due starch gelatinization while slow absorption is found at large times due to the swelling of the sample. A mathematical model is therefore presented enabling to describe the effect of diffusion, swelling and starch gelatinization. Parametric estimation of the model parameters is performed by nonlinear regression techniques providing indications on how to select processing conditions so as to achieve desired characteristics of the final product..

1. Introduction

Chestnut is a traditional food product in Mediterranean countries and is widely employed in food industry. Particular attention has been focused on the application of such fruit because of its nutritional characteristics. Products based on chestnuts can be for example included in the diet of celiac patients due to low gluten content These fruits are characterized by limited shelf-life because of their high water activity and sugar content. Air-drying is therefore performed to achieve physicochemical and microbiological stability (Breisch, 1996). Further processes (shrinkage, color changes) can however occur besides water removal during drying resulting in undesired modifications of certain characteristics of the material. Therefore, it is of great importance to investigate the effect of air-drying processing conditions on the transport of water during rehydration.

Rehydration is traditionally performed by immersion of the dried fruit in water at ambient temperature. Since this process can take long time and does not guarantee an homogeneous distribution of water, the achievement of larger rehydration temperature has been proposed (Lewicki, 1998). Under such conditions, complex phenomena can however take place. At temperature values greater than 60 °C, a large growth in the diffusivity of water is, for example, observed due to starch gelatinization (Stapley et al.,

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1998; Cafieri et al., 2008). Moreover, swelling is enhanced as the rehydration temperature is increased.

In spite of the relevance of such phenomena, empirical or purely Fickian diffusion kinetics are typically employed to fit the data of sorption experiments (Moreira et al., 2008). Particularly, the influence of starch gelatinization on the transport of water during rehydration has not been adequately investigated.

This paper presents an experimental and modeling study of the rehydration process of air-dried chestnuts. Sorption curves are presented for chestnuts dried at 40, 60, and 80 ^{o}C immersed in water at 90 ^{o}C and DSC measurements are performed to characterize the evolution of the gelatinization process during rehydration. In this way, stages of the rehydration process governed by different physical mechanisms are identified. A mathematical model is then formulated enabling to describe the effect of diffusion, swelling and starch gelatinization on the absorption of water in dried chestnuts.

2. Materials and methods

Samples of "Palumna Cultivar" were obtained from local farms in the Campania region, Italy. Drying was carried out on fruits with external shell and weight ranging from 10 to 11 g, at 40, 60 and 80 ^{o}C in a convection oven (Zanussi FCV/E6L3), with an air speed of 0.5 m/s. The chestnut weight was monitored by means of a digital balance (Gibertini E42) and drying was stopped when no appreciable variation in the moisture content was observed. The dried products were then rehydrated by immersion in water at 90 ^{o}C for about 8h and the weight was monitored. All drying and rehydration tests were carried out on 10 chestnuts and replicated three times. Differential scanning calorimetry measurements were performed on a Mettler Toledo calorimeter (mod. TC 15 TA Controller, Switzerland). The samples were weighed directly in DSC aluminum pans and scanned at a rate of 5 ^{o}C/min from 20 to 120 ^{o}C.

3. Experimental analysis of the rehydration process

To qualitatively describe the physical mechanisms governing the transport of water in air-dried chestnuts, a preliminary analysis of the results of rehydration experiments is provided in this section. As representative example, we report in Figure 1, the evolution of the amount of water absorbed during rehydration at 90 ^{o}C by chestnuts previously dried at 80 ^{o}C as function of the square root of time. The choice of employing the square root of time as independent variable is aimed to get information about the transport mechanisms governing the absorption of water. The evolution of the moisture content of materials exposed to a low-molecular solute activity is indeed known to initially exhibit a linear dependence on the square root of time before reaching a constant value (Crank, 1968). Therefore, deviations from such behavior can be assumed to provide indications about the occurrence of further physical mechanisms affecting besides diffusion the transport of water.

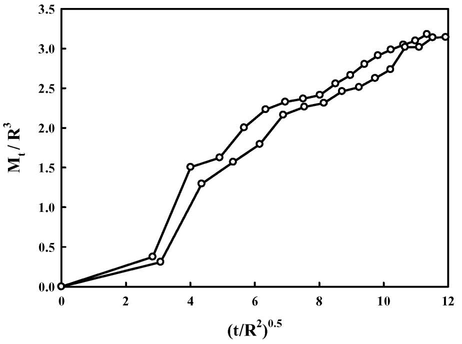

Figure 1. Evolution of the amount of water absorbed by chestnuts dried at 80 °C as function of the square root of time.

The results of Figure 1 clearly indicate a strong deviation from purely diffusive behavior for the absorption of water in air-dried chestnuts. The evolution of the absorbed amount of water as function of the square root of time is S-shaped at small times. In particular, the absorption rate results initially low and rapidly increases at larger time instants.

The growth in the absorption rate observed in the middle region of the diagram must be mainly attributed to the gelatinization of the starchy content of the chestnuts (Attanasio et al., 2004). Starch gelatinization results indeed in a large growth of the diffusivity of water and occurs when moisture concentration exceeds a threshold value depending on the processing temperature. DSC measurements have been therefore performed to characterize the evolution of the gelatinization process during rehydration at different distances from the surface of the sample. As an example, we report in Figure 2 the evolution of the heat flow needed to increase the temperature of a fixed amount of chestnut collected from the centre of the sample at different time instants of the rehydration process. An endothermic peak is found at temperature values ranging between 60 and 80 °C as gelatinization takes place. The area covered by the peak provides a measure of the heat needed to reach complete gelatinization and, hence, identifies the amount of starch not gelatinized. It can be, for example, noted from Figure 2 that gelatinization takes place at the centre of the sample after about 30 min and terminates shortly after 6 hours. Following the illustrated approach has been also proved that gelatinization does not start during the initial 5-10 min of the rehydration process anywhere in the sample. This must be imputed to the low moisture concentration achieved during this time interval. Then, an increase in the rate of the gelatinization process is found as the moisture concentration grows. This justifies the growth in the absorption rate observed in the middle of Figure 1.

Finally, it is important to note that water is slowly absorbed even at large times. Such phenomenon must be attributed to the swelling of the chestnuts. At large times, water is indeed absorbed due to the gradual growth in the sizes of the pores even though no significant concentration gradient is found.

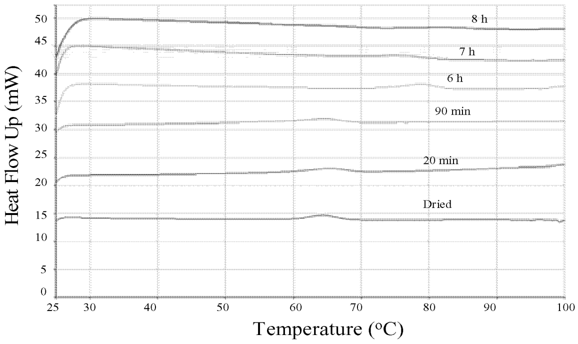

Figure 2. Evolution of the heat flow needed to bring an amount of chestnut collected from the centre of the sample from 25 to 100 oC at different time instants of the rehydration process.

4. Equations

The approach we take to describe the transport of water is to consider the absorption process to be composed of two independent contributions: a diffusion part $M_D(t)$ governed by the Fick's law and a structural part $M_R(t)$ resulting from relaxation of the chestnut matrix (van der Wel and Adan, 1999; Wilde and Shopov, 1994). Therefore, the total weight gain at time t is expressed as follows:

$$M(t) = M_D(t) + M_R(t) \tag{1}$$

Here, $M_D(t)$ is computed by integrating the concentration profiles obtained by solving the following diffusive mathematical model:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right), \quad c(R,t) = c_s(t), \quad \frac{\partial c}{\partial r}(0,t) = 0, \quad c(R,0) = c_0 \tag{2}$$

while MR(t) is expressed as follows:

$$M_R(t) = M_{R,\infty}\left(1 - \exp\left(t / \tau_R\right)\right) \tag{3}$$

with τ_R denoting the characteristic time of the relaxation process and $M_{R\infty}$ the amount of water absorbed after infinite time due to the only effect of swelling.

The formulation (1)-(3) accounts for the influence of diffusion and swelling on the transport of water. However, strong deviations from purely diffusive behavior are also initially observed due to the slow establishment of equilibrium at the surface and a rapid growth in the absorption rate is detected at intermediate times as starch gelatinization takes place. The approach here followed to describe small times deviations from purely diffusive behavior is to assume that the surface concentration c_s takes a finite time interval to reach its asymptotic value (Van der Wel and Adan, 1999). Therefore, c_s in (2) is expressed as follows:

$$c_S(t) = c_f\left(1 - \exp\left(t/\tau_s\right)\right) \qquad (4)$$

where c_f is the surface concentration of the chestnut under equilibrium conditions and τ_s denotes the characteristic time needed to reach such a value. It must be remarked that c_f does not represent the concentration actually observed in the chestnut at infinitely large times. The asymptotic water concentration results, in accordance with the formulation (1)-(3), from the sum of c_f and the concentration $M_{R\infty}/V_c$, V_c being the chestnut volume, absorbed after infinite time due to the only effect of swelling.

To account for the rapid growth in the absorption rate due to starch gelatinization, a dependence of the diffusion coefficient on the water concentration is also assumed. In particular, the following step function for the diffusion coefficient is employed:

$$D(c) = \begin{cases} D_1 & c \leq c^* \\ D_2 & c > c^* \end{cases} \qquad (5)$$

where D_1 and D_2 denote the diffusion coefficient value before and after gelatinization respectively and c^* is the critical water concentration at which gelatinization occurs.

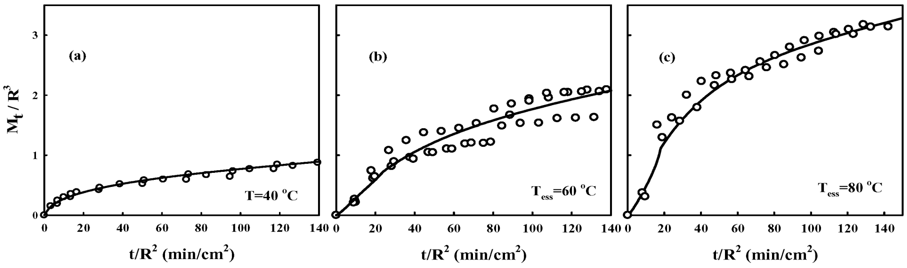

Figure 3. Comparison between the evolution of the amount of absorbed water predicted by the model (1)-(5) with parameter values reported in Table-1 and the results of rehydration tests for chestnuts previously dried at 40, 60, 80 °C.

In order to implement the model (1)-(5), the following unknown parameters must be estimated: $M_{R\infty}$ c_f, c^*, τ_R, τ_s, D_1, D_2. $M_{R\infty}$ can be however expressed as difference between the amount of absorbed water found experimentally after large times and the amount of water c_fV_c predicted by solving the model (2), (4), (5). Nonlinear regression techniques have been applied to estimate the remaining parameters. A comparison between model predictions achieved with the estimated parameters (see Table-1) and experimental data is shown in Figure 3. It is apparent that the formulated mathematical model satisfactory covers the available experimental data. The presented results suggest a significant dependence of the rehydration behavior on the thermal history of the sample. A reduction of D_1 and D_2 is observed as the drying temperature is increased. Also, the characteristic time of the relaxation process decreases at larger drying temperature indicating a growth in the water absorbed by swelling.

Table 1. Estimated model parameters

	D_1 x 10^8 m^2/s	**D_2 x 10^8 m^2/s**	**c^* g/cm^3**	**c_f g/cm^3**	**τ_s min**	**τ_R min**
40 °C	0.98±0.037	4.94 ± 1.85	0.075±0.013	0.073±0.012	1.75±0.37	642±16.9
60 °C	0.96± 0.06	3.31 ± 0.3	0.077±0.004	0.29±0.04	52.74±9.02	371±14.41
80 °C	0.63 ± 0.05	3.32 ± 0.42	0.084±0.005	0.4826±0.02	47.72±2.64	188±23.96

5. Conclusions

An experimental and modeling study of the rehydration process of air-dried chestnuts was performed. Chestnuts previously dried at 40, 60 and 80 °C were rehydrated by immersion in water at 90 °C and sorption curves were constructed. The evolution of the absorbed amount of water was invariably found to exhibit deviation from purely diffusive behavior. These deviations can be imputed to the occurrence of swelling and starch gelatinization. The effect of starch gelatinization process was particularly characterized by DSC measurements. A model was formulated accounting for diffusion, starch gelatinization and relaxation of the chestnut matrix. Satisfactory agreement between model predictions and experimental data was achieved.

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