

Modeling of Water Sorption Kinetics in Spaghetti During Overcooking

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ABSTRACT

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The organoleptic changes of pasta during overcooking are strongly related to the rate at which water molecules penetrate the pasta matrix once the optimal cooking conditions are reached. A model to describe water sorption kinetics during the overcooking stage is presented. The model has been developed assuming that overcooking starts once the central core disappears and that during this stage sorption kinetics are governed by

the pasta matrix relaxation rate. To validate the model, water sorption tests were performed at 10–100°C. A good agreement between the model predictions and the experimental data was obtained. Based on these results, the main matrix relaxation time can be used to compare behavior during overcooking of pastas with different compositional and technological variables.

Manufacturing pasta while retaining the organoleptic properties from the optimal cooking time during overcooking has driven many scientists to focus their attention on the physical and chemical modifications occurring during the cooking process. Many articles can be found in the literature dealing with this subject (Zeleznač and Hoseney 1987, Galvez et al 1994, Dincer and Esin 1996). Some concerned the measurement of the degree of starch gelatinization (Shetty et al 1974) and its correlation with pasta cooking quality (Edwards et al 1993), others concerned the determination of relationships existing among raw materials, process variables, and cooking performances (Marshall and Wasik 1974, Dexter et al 1983, D'Egidio et al 1990, Grant et al 1993, Novaro et al 1993, Kovacs and Varga 1995, Köksel et al 1996). Some authors analyzed cross sections of spaghetti with cross-polarized light and showed the presence of a traveling discontinuity separating a central core from an outer swollen region (Grzybowski and Donnelly 1977). Nuclear magnetic resonance (NMR) analysis showed that the sharp front moving toward the center of the sample is related to a discontinuity of the water concentration profile (Hills et al 1996). Starch gelatinization kinetics during cooking have also been investigated using differential scanning calorimetry by Riva et al (1991), who reported that the phenomenon can be described by means of a first-order kinetic equation. From the literature survey, it appears that complex phenomena such as matrix relaxation, melting kinetics of starch crystals, and diffusion of water molecules through the pasta matrix contribute to the behavior of pasta during the cooking process.

In the present article, a model able to predict the water sorption kinetics in spaghetti during overcooking has been proposed. The approach adopted to derive the model is analogous to that used to describe anomalous diffusion in polymers (Del Nobile et al 1994). The model is based on the assumption that once the optimal cooking conditions have been reached (commonly when the central core disappears) (Dexter et al 1983, Edwards et al 1993), water sorption kinetics are controlled by the matrix relaxation rate. To validate the model, water sorption kinetics in spaghetti were evaluated at 10–100 °C.

MODELING

During the early stage of the cooking process, the pasta temperature suddenly reaches that of the surrounding water, inducing a glassy-rubbery transition in the pasta matrix. However, due to

both the low initial water content and the negligible amount of water sorbed during the thermal transient, the matrix crystalline level does not change substantially. At a later stage, water penetrates the matrix, lowering the melting temperature of the starch crystals below that of the boiling water (Lelievre 1973, 1976), melting most of the ordered domains present into the sample and reducing the degree of cross-linking. As a consequence, more water penetrates the matrix (Lelievre 1976), resulting in a significant softening of pasta (Edwards et al 1993).

Considering the cooking process, it follows that water uptake kinetics depend on three phenomena: 1) the ability of water to diffuse through the matrix; 2) the melting kinetics of the crystalline domains; and 3) the rate at which the matrix moves toward a new conformation (matrix relaxation rate). The first two phenomena are mainly responsible for the water penetration rate at the initial stage of the cooking process: the time at which the unpenetrated central core disappears and all the starch crystals melt (first stage). The third phenomenon controls the water uptake kinetics until a pseudoequilibrium state is reached: before carbohydrate hydrolysis and amylose depletion begin (second stage) (Dexter et al 1983, Grant et al 1993). Therefore, water sorption kinetics during overcooking can be modeled as a matrix relaxation phenomenon.

As proposed by Thomas and Windle (1982), a dynamic equilibrium is established between the external water and that adsorbed into the matrix. When the amount of sorbed water is lower than that absorbed at the pseudoequilibrium state (end of the second stage), an osmotic pressure exerted by the pasta matrix, acts on the water molecules raising the chemical potential to that of the pure water. The osmotic pressure is counterbalanced by an isotropic tensile stress within the matrix exerted by the water molecules. Due to matrix relaxation, the osmotic pressure gradually decreases, leading to a reduction of the sorbed water chemical potential. More water penetrates to reequilibrate the water chemical potential inside and outside the pasta. This process continues until the osmotic pressure vanishes (pseudoequilibrium conditions are reached).

To predict the rate at which the matrix releases the isotropic tensile stress, a constitutive equation relating matrix deformation to the applied stress must be established. In principle, any of the constitutive equations proposed in literature to describe the viscoelastic behavior of a macromolecular system could be used. We chose the Maxwell model because it is characterized by one relaxation time. In fact, the Maxwell model has been proposed to describe the viscoelastic behavior of thermoplastic polymers. Considering that, during the second stage, the pasta matrix is only lightly cross-linked, it also seems reasonable to adopt this model for our system. The constitutive equation of a Maxwell element (Rosen 1982) is:

$$\frac{d\epsilon(t)}{dt} = \frac{d\sigma(t)}{dt} \cdot \frac{1}{E} + \frac{\sigma(t)}{\eta} \quad (1)$$

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where: $\epsilon(t)$ = matrix deformation at time t ; E = elastic modulus; η = viscosity.

Assuming the additivity of the volumes on mixing, we can demonstrate that matrix deformation is related to sorbed water volume fraction as:

$$\epsilon(t) = \frac{v_1(t)}{1 - v_1(t)} \quad (2)$$

Substituting equation (2) in equation (1) produces:

$$\frac{1}{1 - [v_1(t)]^2} \cdot \frac{dv_1(t)}{dt} = \frac{d\sigma(t)}{dt} \cdot \frac{1}{E} + \frac{\sigma(t)}{\eta} \quad (3)$$

The parameters η and E can, in principle, depend on the water volume fraction; however, in this study, they have been assumed constant.

Because Equation 3 has two variables, $v_1(t)$ and $\sigma(t)$, a relationship between them needs to be established to solve the problem. By definition, the change of the water chemical potential with respect to a reference state, when both pressure and composition have been modified is:

$$\mu_1 - \mu_1^0 = \Psi + \xi \quad (4)$$

where μ_1 is the sorbed water chemical potential; μ_1^0 is the pure water chemical potential (reference state); Ψ is the change of the pure water chemical potential due to a variation of the applied pressure; ξ is the change of the pure water chemical potential due to a variation of composition. Assuming that the molar volume of pure water is constant with pressure, it can be easily demonstrated that Ψ equals:

$$\Psi = \sigma \cdot \bar{V}_1 \cdot N_a \quad (5)$$

where: N_a is the Avogadro's number; \bar{V}_1 is the water molecular volume.

To evaluate ξ , a constitutive equation describing the sorption isotherm of the water-spaghetti system must be established. Many relationships, both empirical and theoretical, are reported in literature (Dincer and Esin 1996, Rizvi 1986). In the present study, the equation developed by Flory (1953) to describe the mixing of a linear polymer with a low molecular weight compound when there are no specific interactions between the two components of the mixture, was used:

$$\xi = R \cdot T \cdot [\ln v_1 + (1 - v_1) + \chi \cdot (1 - v_1)^2] \quad (6)$$

where R is the universal gas constant; T is the absolute temperature; and χ is the Flory-Huggins interaction parameter.

Pasta is a complex heterogeneous mixture of cross-linked gluten, starch, and lipids, and specific interactions between water and the pasta matrix exist (bound water). Therefore, the theoretical arguments used to derive Equation 6 are not valid for the system under investigation. However, the model proposed by Flory could be used to describe the water-pasta system as an empirical equation, if it is assumed that the bound water is negligible compared with the total amount of sorbed water (Dincer and Esin 1996), and that the upper part of the water sorption isotherm of starch-based products has an upward concavity (Dincer and Esin 1996, Rizvi 1986). In this case, the interaction parameter χ loses the original physical meaning and must be considered as a fitting parameter.

Substituting Equations 5 and 6 in Equation 4, and recalling the assumption that $\mu_1 = \mu_1^0$:

$$0 = \frac{\sigma(t) \cdot \bar{V}_1 \cdot N_a}{R \cdot T} + \ln[v_1(t)] + [1 - v_1(t)] + \chi \cdot [1 - v_1(t)]^2 \quad (7)$$

Combining equations (3) and (7) one obtains:

$$\frac{dv_1(t)}{dt} = \frac{-\left\{\ln[v_1(t)] + [1 - v_1(t)] + \chi \cdot [1 - v_1(t)]^2\right\}}{\eta \cdot \frac{\bar{V}_1 \cdot N_a}{R \cdot T} + \tau \cdot \left\{\frac{1}{v_1(t)} - 1 - 2 \cdot \chi \cdot [1 - v_1(t)]\right\}} \quad (8)$$

The resulting differential equation has three fitting parameters:

χ , $A_1 = \eta \cdot (\bar{V}_1 \cdot N_a / R \cdot T)$, and the matrix relaxation time $\tau = \eta/E$

Equation 8 was integrated numerically using a fourth-order Runge-Kutta formula (Press et al 1989) and used to fit the experimental data.

MATERIALS AND METHODS

Commercial spaghetti (diameter 1.7 ± 0.5 mm) from a single commercial source (Barilla) was used in all the experiments.

Sorption tests were performed using 5-cm samples. Culture tube containing ≈ 70 cm³ of distilled water were equilibrated in a thermostated bath ($\pm 0.5^\circ\text{C}$ accuracy). Samples were immersed separately in tubes. At a given time, the sample was removed from the tube, rapidly blotted, and weighed (Mettler AE 240). Diameter and length were measured. The sample external diameter was measured with a chatetometer (Galileo, Florence, Italy) with an accuracy of 1/760 mm; the length was measured with a gauge with an accuracy of 1/20 mm.

Samples were conditioned in distilled water for different times at 40 and 100°C to determine the position of the central core with an optical microscope (Polyvar, Reichert-Jung) equipped with cross-polarized light. At a fixed time, the sample was extracted from the culture tube and immersed in a mixture of ice and water to slow water migration. It was gently blotted with filter paper and then a thin slice ≈ 1 mm was cut with a saw provided with a circular sharp blade 0.2 mm thick. The slice was observed under the optical microscope and photographs of the cross section were taken.

RESULTS AND DISCUSSIONS

Water sorption kinetics obtained at 10–100°C are shown in Figs. 1 and 2. For temperatures $\leq 40^\circ\text{C}$, water uptake increased linearly with the square root of time and then suddenly leveled off to an asymptotic value. A rather different behavior was observed at $>40^\circ\text{C}$, where the starch gelatinization process superimposes the water diffusion process. At temperatures where gelatinization does not occur, the weight of pasta increased $<100\%$, while at $>50^\circ\text{C}$, water increments as high as 500% were measured.

Figure 3 shows a sequence of photographs of the transverse section of spaghetti taken at different stages of the sorption process. At 100 and 40°C, the central core is separated by a sharp boundary forming an outer shell. Figure 4 shows the core diameter evaluated from Fig. 3, plotted as a function of the hydration time at 40 and 100°C. At 40°C (when starch gelatinization does not occur), the hydration kinetics stop when the internal core disappears.

Figure 5 shows the normalized water volume gain versus the normalized water weight gain at 60, 80, and 100°C. A direct proportionality exists between them, suggesting that pasta and water volumes are additive with mixing. This evidence would confirm the hypothesis of Equation 2.

Figure 6 shows the model that best fits the experimental data collected at 100°C. Because the model was developed to describe water sorption kinetics during overcooking, data before the central core disappears (11.5 min, Fig. 4) were not considered. Moreover, to account for the water weight gain related to the diffusion process, a constant value, K , has been subtracted from the total amount of sorbed water. K equals the equilibrium volume fraction measured at 40°C, where it is reasonable to exclude any influence of starch gelatinization on water sorption kinetics.

To further explore the validity of the model, its predictive ability was tested at 60 and 80°C, where, as at 100°C, starch gelatinization and matrix relaxation take place while water molecules penetrate the matrix. At these two temperatures, K was evaluated as previously described, while the time at which the central core disappears, t^* , was estimated by interpolating the data obtained at 10, 20, 40, and 100°C. At the first three temperatures, t^* was determined from the sorption kinetic curves, while at 100°C, the time at which the core disappears was evaluated from the data reported in Fig. 4. Figure 7 shows t^* as a function of reciprocal temperature (K). The data are

well correlated with an Arrhenius type equation. The values of t^* obtained at 60 and 80°C are 36 and 20 min respectively. The models with the best fit for the tests performed at 60 and 80°C are shown in Figs. 8 and 9, respectively. Again, the agreement between experimental data and the model predictions seem to be satisfactory.

Table I gives the model parameters estimated at three temperatures. Figure 10 shows τ as a function of the inverse of absolute temperature. The data seem to be well correlated with an Arrhenius type equation, as one would expect for an activated process like matrix relaxation.

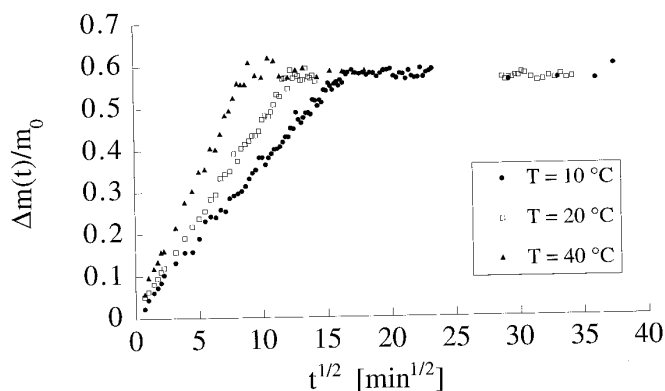


Fig. 1. Water uptake vs. square root of time at 10, 20, and 40°C.

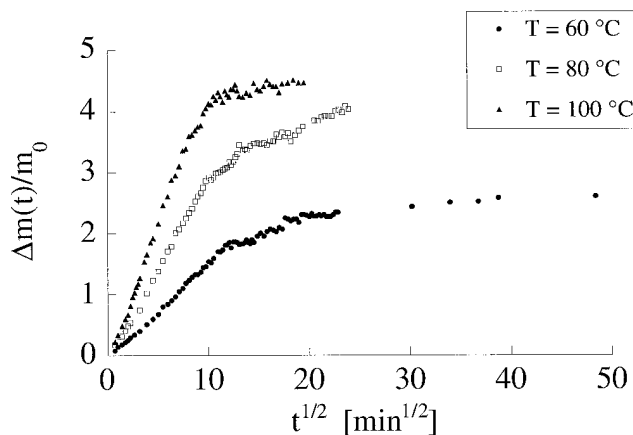


Fig. 2. Water uptake vs. square root of time at 60, 80, and 100°C.

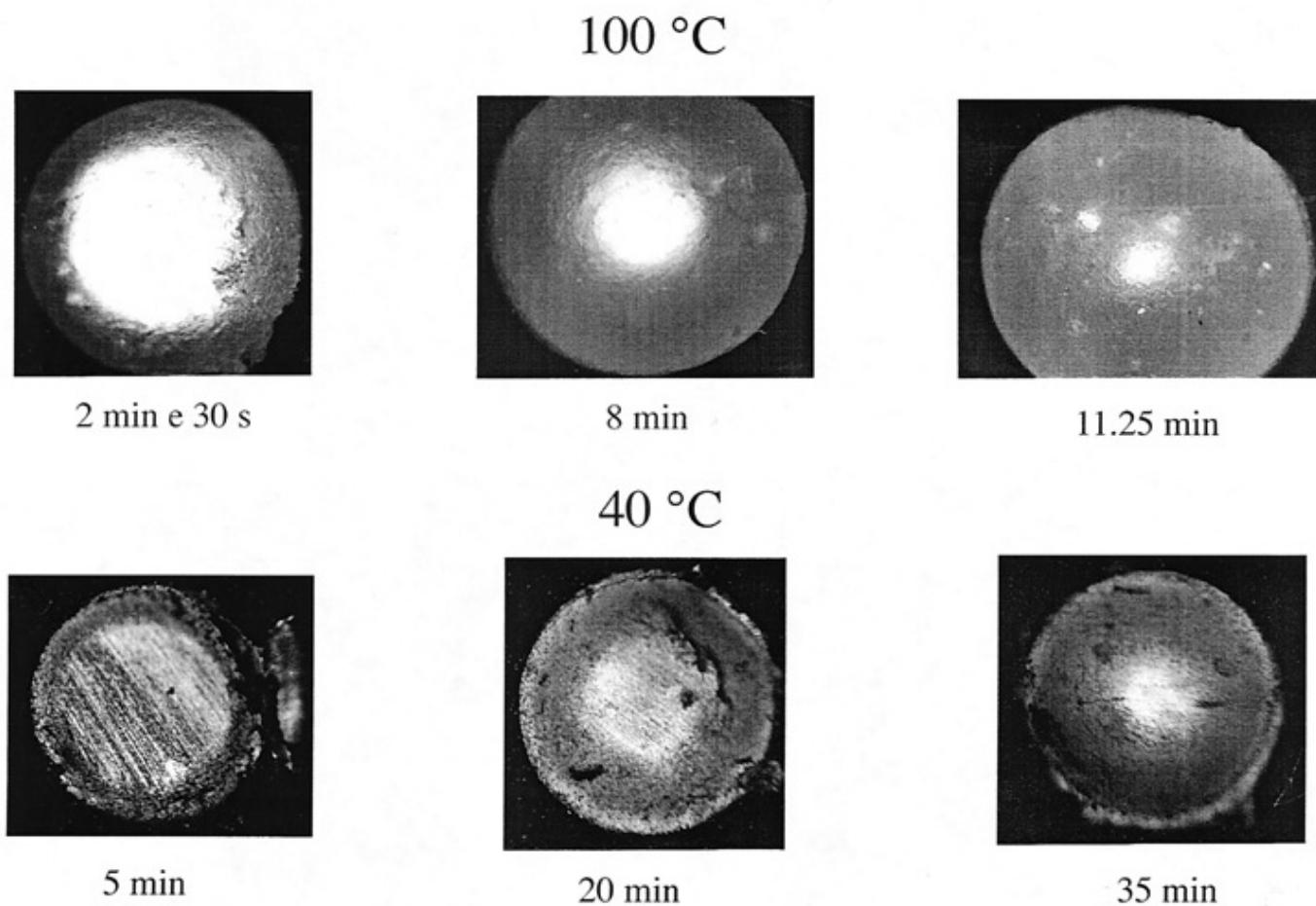


Fig. 3. Cross sections of samples taken during the sorption process.

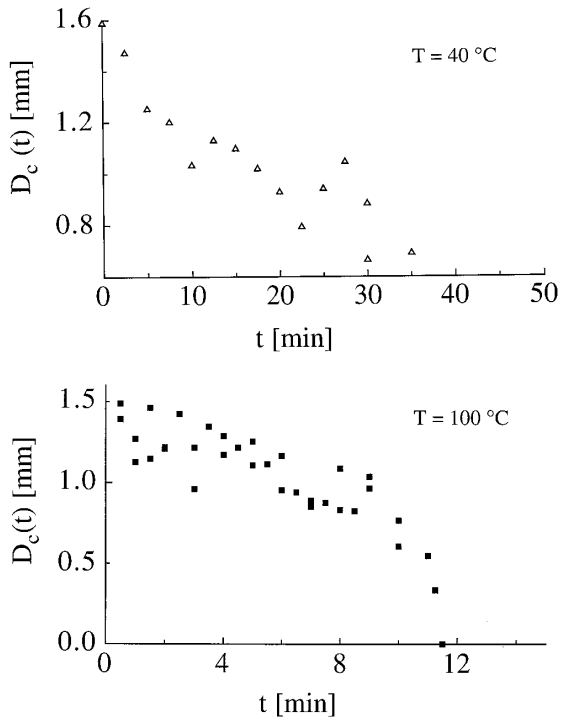


Fig. 4. Diameter of the core (D_c) from cross section vs. time at 40 and 100°C.

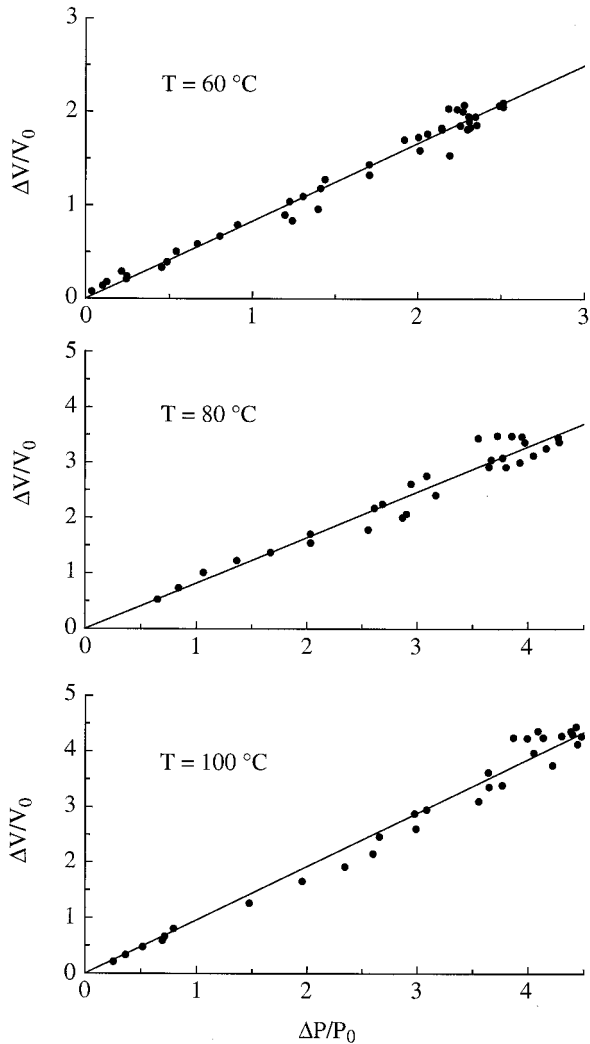


Fig. 5. Normalized volume gain vs. normalized wt. gain at 60, 80 and 100°C.

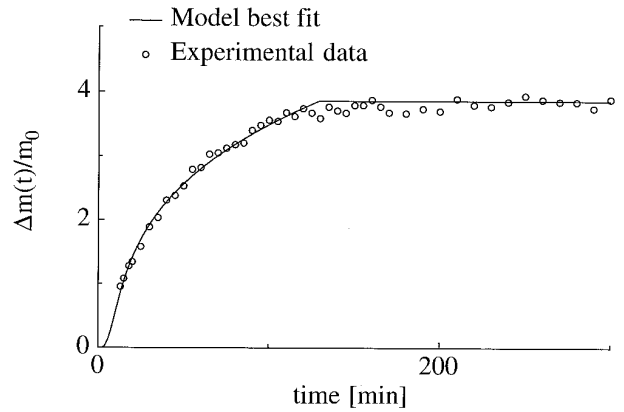


Fig. 6. Water uptake vs. time at 100°C. Curve represents best fit for model (Eq. 8).

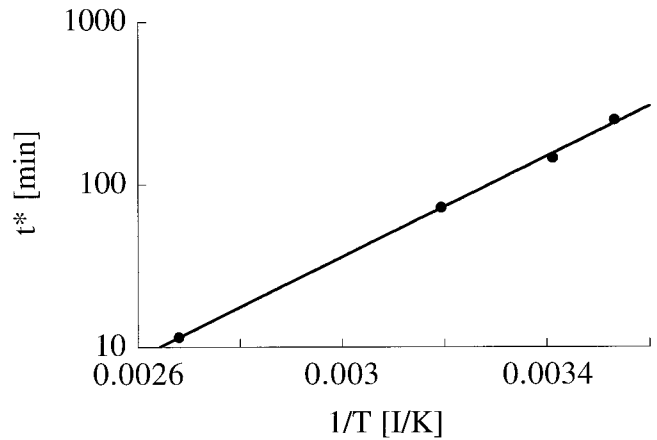


Fig. 7. Time central core of pasta disappears vs. inverse of absolute temperature.

TABLE I
Values of A_1 , χ , and τ Obtained by Fitting Experimental Data at 60, 80, and 100°C

Temp. (°C)	A_1 (min)	τ (min)	χ
60	4.30 ± 0.17	7.88 ± 0.260	$0.593 \pm 1.06 \cdot 10^{-3}$
80	$0.729 \pm 2.73 \cdot 10^{-2}$	3.47 ± 0.115	$0.553 \pm 6.27 \cdot 10^{-4}$
100	$0.429 \pm 7.20 \cdot 10^{-2}$	1.69 ± 0.129	$0.517 \pm 8.78 \cdot 10^{-3}$

Assuming that the characteristic time of the diffusion process is negligible compared with that of matrix relaxation, and neglecting the bound water compared with the total amount of sorbed water, represent the major limitations to an extension of the proposed model to a general case. Where these assumptions are satisfied, as in the samples analyzed in the present work, a good agreement between the experimental data and the model predictions was found.

CONCLUSIONS

A model to predict water sorption kinetics during overcooking is proposed. The model is based on the assumption that once the unpenetrated central core disappears, the water sorption kinetic is controlled by the matrix relaxation rate.

The capability of the model to fit the experimental data at 60, 80 and 100°C was quite good. Moreover, the evaluated relaxation time changes with temperature according to an Arrhenius type equation. This evidence seems to support the idea that matrix relaxation is mainly responsible for pasta overcooking performances. Based on these results, we can use the matrix relaxation time as an objective measure of the rate at which pasta properties change once the

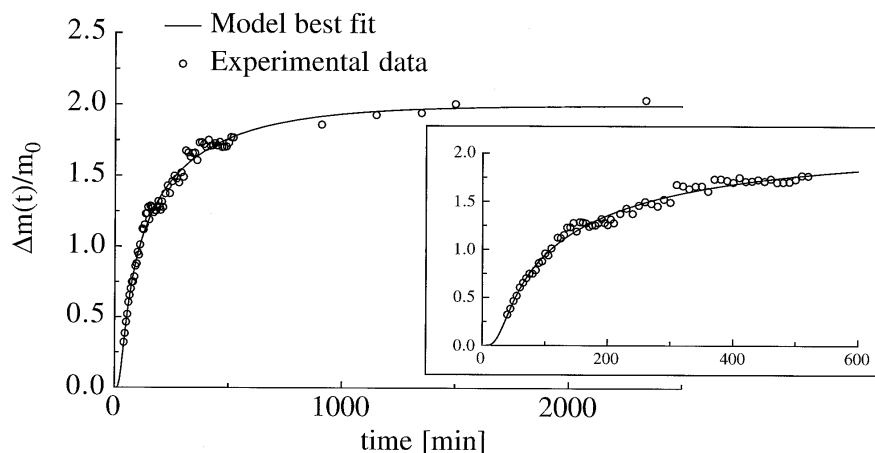


Fig. 8. Water uptake vs. time at 60°C. Curve represents best fit for model (Eq. 8). Inset represents magnification of the first part of the plot.

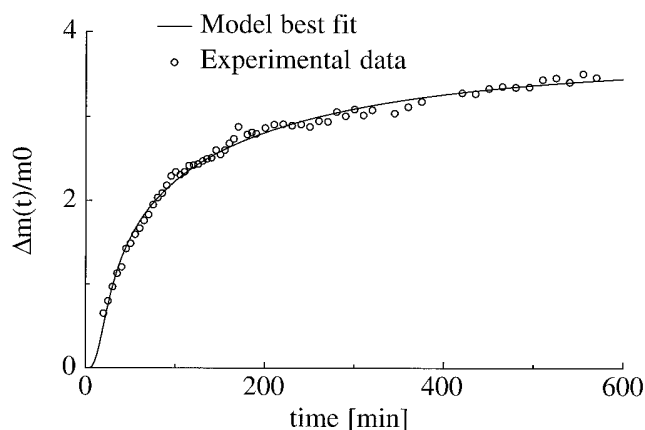


Fig. 9. Water uptake vs. time at 80°C. Curve represents best fit for model (Eq. 8).

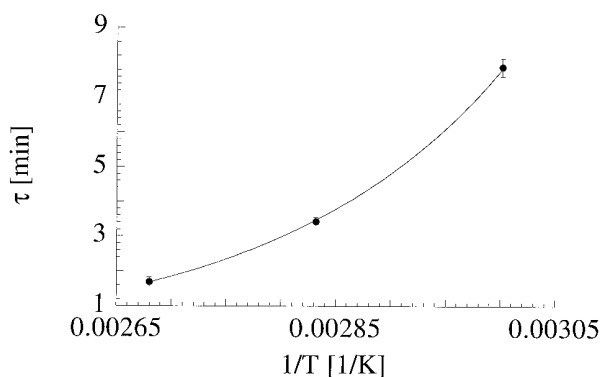


Fig. 10. Matrix relaxation time vs. inverse of absolute temperature.

optimal cooking conditions are reached. In fact, the longer the relaxation time, the less the rate of water uptake during the overcooking stage and, therefore, the better the pasta performance.

LITERATURE CITED

D'Egidio, M. G., Mariani, B. M., Nardi, S., Novaro, P., and Cubadda, R. 1990. Chemical and technological variables and their relationships: A predictive equation for pasta cooking Quality. *Cereal Chem.* 67:275-281.

Del Nobile, M. A., Mensitieri, G., Netti, P. A., and Nicolais, L. 1994. Anomalous diffusion in poly-ether-ether-ketone (PEEK). *Chem. Eng.*

Sci. 49:633-644.

Dexter, J. E., Matsuo, R. R., and Morgan, B. C. 1983. Spaghetti stickiness: Some factors influencing stickiness and relationship to other cooking quality characteristics. *J. Food Sci.* 48:1545-1551.

Dincer, T. D., and Esin, A. 1996. Sorption isotherms for macaroni. *J. Food Eng.* 27:211-228.

Edwards, N. M., Izydorczyk, M. S., Dexter, J. E., and Biliaderis, C. G. 1993. Cooked pasta texture: Comparison of dynamic viscoelastic properties to instrumental assessment of firmness. *Cereal Chem.* 70:122-126.

Flory, P. J. 1953. Statistical thermodynamics of polymer solutions. Pages 495-512 in: *Principles of Polymer Chemistry*. Cornell University Press: Ithaca, NY.

Galvez, F. C. F., Resurreccion, A. V. A., and Ware, G. O. 1994. Process variables, gelatinized starch and moisture effects on physical properties of mungbean noodles. *J. Food Sci.* 59:378-386.

Grant, L. A., Dick, J. W., and Shelton, D. R. 1993. Effects of drying temperature, starch damage, sprouting and additives on spaghetti quality characteristics. *Cereal Chem.* 70:676-684.

Grzybowski, R. A., and Donnelly, B. J. 1977. Starch gelatinization in cooked spaghetti. *J. Food Sci.* 42:1304-1305.

Hills, B. P., Bambonneau, F., Quantin, V. M., Gaudet, F., and Belton, P. S. 1996. Radial NMR microimaging studies on the rehydration of extruded pasta. *J. Food Eng.* 27:71-86.

Köksel, H., Çelik, S., and Tuncer, T. 1996. Effects of gamma irradiation on durum wheat and spaghetti quality. *Cereal Chem.* 73:506-509.

Kovacs, E., and Varga, J. 1995. Studio sulla qualità di pasta alimentare a base di amido di mais. *Tec. Molitoria Novembre*:1206-1211.

Lelievre, J. 1973. Starch gelatinization. *J. Appl. Polym. Sci.* 18:293-296.

Lelievre, J. 1976. Theory of gelatinization in a starch-water-solute system. *Polymer* 17:854-858.

Marshall, S., and Wasik, R. 1974. Gelatinization of starch during cooking of spaghetti. *Cereal Chem.* 51:146-147.

Novaro, P., D'Egidio, M. G., Mariani, B. M., and Nardi, S. 1993. Combined effect of protein content and high-temperature drying systems on pasta cooking quality. *Cereal Chem.* 70:716-719.

Press, W. H., Flannery, B. P., Teukolsky, S. A., and Vetterling, W. T. 1989. Numerical recipes in Pascal. Pages 602-607 in: *Integration of Ordinary Differential Equations*. Cambridge University Press: England.

Riva, M., Piazza, L., and Schiraldi, A. 1991. Starch gelatinization in pasta cooking: Differential flux calorimetry investigations. *Cereal Chem.* 68:622-627.

Rizvi, S. S. H. 1986. Thermodynamic properties of foods in dehydration. Pages 133-214 in: *Engineering Properties of Foods*. M. A. Rao and S. S. H. Rizvi, eds. Marcel Dekker: New York.

Rosen, S. L. 1982. Linear viscoelasticity. Page 240 in: *Fundamental Principles of Polymeric Materials*. Wiley & Sons: New York.

Shetty, R. M., Lineback, D. R., and Seib, P. A. 1974. Determining the degree of starch gelatinization. *Cereal Chem.* 51:364-375.

Thomas, N. L., and Windle, A. H. 1982. A theory of Case II diffusion. *Polymer* 23:529-542.

Zelezna, K. J., and Hosney, R. C. 1987. The glass transition in starch. *Cereal Chem.* 64:121-124.

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