Application of Biopolymers in Designing Completely Soluble Materials For Food Product Packaging

Roxana Puscaselu (Gheorghita)*
Stefan cel Mare University

Sonia Amariei
Stefan cel Mare University

ABSTRACT

The aim of this study was to create a completely hydrosoluble edible films based on biopolymers that can be used as packaging material for powdered foods. 10 edible films were obtained from various mixtures of hydrocolloids (agar, starch, sodium alginate) plasticized with glycerol and water. To assess their solubility, it was used the Peleg model which confirmed that increasing the temperature of the hydration medium, increases the water absorption rate. The sample obtained from agar and starch was less hydrophilic than sample with a high amount of sodium alginate, which was completely soluble after 3 minutes maintenance in 20° water. To determine the characteristics of novel food packaging material it is important to know the behavior of these hydrocolloids. The completely hydrosolubility of biofilm obtained from a higher amount of sodium alginate in a very short time successfully qualifies it for producing environmentally friendly edible packaging materials for various products which can be consumed with the product, resulting zero waste.

KEY WORDS

Packaging, Hydrosoluble, Biopolymers, Peleg Model

*Roxana Puscaselu (Gheorghita)
Corresponding Author
roxana.puscaselu@fia.usv.ro

INTRODUCTION

Environmental problems caused by conventional oil-based packaging have forced industry to constantly seek new solutions so as to remove its harmful effects. Biofilms from polysaccharides, proteins or lipids have been extensively used since they offer obvious benefits: biodegradability, biocompatibility, regenerability, wide spread, and low cost. [1] Furthermore, biopolymers not only improve food quality and food security, but they also extend the shelf life. In addition, biofilms are completely edible, can prevent gas or vapor absorption, improve mechanical properties, are hydrosoluble, and can provide a pleasant gloss and appearance due to their optical characteristics. [2] They can enrich the product's nutritional characteristics through the fiber intake they contain.

Edible packages can be dissolved through cooking or simply immersed in hot water; they can be mixed up with various natural substances: preservatives, antioxidants, nutrients, and caffeine or oral hygiene substances. They can be mixed up with pharmaceutical substances in order to obtain strips that can be directly swallowed without water addition, suitable for patients with dysphagia problems. [3] Studies have been conducted in order to obtain edible and soluble biofilms, used as packaging material for melted cheese, sugar, spices, ketchup, candies, instant drinks, sauces and even in cosmetics for facial masks.

The novelty of this study is to design a completely hydrosoluble packing material used for powder vegetables or instant drinks, and to determine the solubility of biofilms made from agar, starch and sodium alginate, plasticized with water and glycerol. Agar is a polysaccharide extracted from marine red algae with a wide applicability in food, biotechnology, medicine, and pharmaceutical industries, [4] and it has an excellent ability to form biofilms with improved properties. Starch is one of the most extensively studied hydrocolloid, mainly due to its advantages: low cost, high availability, and complete compostability without toxic residues traces. [5] Alginates are used for their high thickening capacity, stabilization, emulsion suspension, film or gel forming; they are non-toxic, biodegradable, biocompatible and inexpensive. [6] Glycerol has been used for its plasticizing effect in order to improve film flexibility due to its ability to reduce the hydrogen bonds between the polymer chains. Plasticizers prevent the film breaking or cracking during handling or storage. [7]

Peleg model has been used to describe dried foods, especially dehydrated fruits and vegetables. It provides accurate information about water absorption and moisture content at different time of immersion, which is an important aspect for detecting the film hidrophobicity, and also for the interactions between matrix and water molecules. [8] There are many mathematical models that describe water isotherms; yet, no one provides accuracy, and no one can be applied to the entire food category. [7]

The findings of this study indicate the feasibility of using these biofilms as powdered food packaging material, since they are completely solvable in hot water and they are recommended for human consumption.

MATERIALS AND METHODS

Biofilms were made from agar, starch from wheat, sodium alginate, and glycerol purchased from Sigma Aldrich company.

Films were obtained by casting method from different amounts of biopolymers and glycerol in a total amount of 4g and 150 ml distilled water; the solutions were maintained for 30 minutes at 90°C under vigorous stirring, then were poured onto the silicone support surface and kept at room temperature until completely dried.

Adhesion of silicone support, appearance, taste and smell were evaluated. The color was determined by CieLAB method using the Chroma Meter CR 400 colorimeter (Minolta, Tokyo, Japan). The thickness was evaluated using the Mitutoyo digital micrometer, the result being set as the arithmetic means for at least five different areas.

The determination of solubility is important when we want to use the film as packaging material, since its destination can be appreciated for products with high/low moisture content or for completely hydro soluble packaging, as presented in the present paper. To evaluate solubility or moisture capacity, determinations such as moisture content, swelling ratio, water solubility, Peleg model and rehydration ratio were made. Regarding the safety of product ingestion, the trace of metals was assessed using an Agilent Inductively coupled plasma mass spectrometry ICP-MS.

Peleg model: the mathematical modeling of hydration process is important for the design and optimization of technological food processing operations. Peleg model is a non-exponential and empiric model with parameters that have practical significance for hydration kinetics interpretation. [9]

Peleg model [10] describes equation (1) as follows:

$$M(t) = M_0 + t/(k_1 + k_2 t) \qquad (1),$$

where $M(t)$ is moisture content after t time of immersion, $M(0)$ is initial moisture content, k_1, k_2 are constants whose units of measurement will correspond to the unit of measure $M(t)$, respectively $M(0)$ (here k_1 - min% $^{-1}$ and k_2 -% $^{-1}$) [10]; k_1 constant refers to mass transfer rate: the lower the amount of the transfer, the higher the initial absorption rate. It has negative values during desorption and corresponds to the initial water absorption rate; k_2 constant indicates the maximum water absorption capacity. [7]

Equation (1) can be transformed into a linear form equation whose graphic representation provides a simple way to test the applicability of this model in order to determinate absorption and calculate parameters by linear regression. [10]

The rehydration capacity of dehydrated products can be determined by the rehydration ratio (RR) (3):

$$RR = (X+1)/(X_i-1) \qquad (2),$$

where X/X_i is the moisture content after immersion/initial moisture content, (g/g db). [11] For determination, the film samples were dried according to the method described by Rhim, Park, & Ha (2012) [12]: 3x3 cm film strips were weighted and dried at 110°C/24h and then reweighted. The result was expressed according to the moisture content formula.

The dried film was immersed into distilled water at the temperatures of 20°C, 40°C, 60°C, 80°C, and 100°C for different periods of time (30 seconds to 10 minutes). Only the values obtained for 20°C and 40°C were used, since at higer values the film samples were completey solubilized, and their reweighting was thus impossible.

For swelling ratio determination, film samples were immersed in water at 22°C for 30 seconds to 10 minutes.

The film strips were weighted after and before immersion, and the swelling ratio values were determined according to the (5) formula:

$$SR, (\%) = [(W_t - W_0)/W_0] \times 100 \qquad (3),$$

where W_0/W_t represents the initial film weight/film weight after t time of immersion, (g) [13]

The obtained values are of interest as they highlight not only the biofilms hydration capacity, but also their complete solubility.

Water solubility was determined by weighting the film samples before and after immersion in distilled water (tank with 50 ml water at room temperature) and slight homogenization. The initial film sample was dried according to the method described by Rhim, Park, & Ha (2012)

Table 1: The characteristics of tested film samples.

Assay	Thickness (μm)	Moisture content, MC, (%)	Water solubility, WS, (%)	Color		
				L*	a*	b*
P1	33 ± 1.54	18.52 ± 0.02	41.75 ± 0.02	91.58 ± 0.05	-5.43 ± 0.03	15.41 ± 0.19
P2	29.6 ± 2.19	23.05 ± 0.005	40.27 ± 0.01	90.6 ± 0.780	-5.3 ± 0.13	16.49 ± 1.48
P3	29.4 ± 1.51	25.9 ± 0.1	26.02 ± 0.02	90.82 ± 0.76	-5.15 ± 0.11	16.04 ± 0.98
P4	30.6 ± 1.51	19.13 ± 0.01	48.52 ± 0.02	92.94 ± 0.38	-5.69 ± 0.02	12.90 ± 0.77
P5	30 ± 1.87	24.2 ± 0.2	31.2 ± 0.01	92.62 ± 0.46	-5.55 ± 0.05	13.48 ± 0.56
P6	40.6 ± 1.94	18.52 ± 0.05	61.75 ± 0.02	90.59 ± 0.67	-5.3 ± 0.67	12.53 ± 1.11
P7	35 ± 1.58	16.81 ± 0.01	complete solubilization	91.82 ± 0.25	-5.47 ± 0.02	14.06 ± 0.27
P8	34.6 ± 1.51	11.63 ± 0.02	35.82 ± 0.01	90.71 ± 0.32	-5.34 ± 0.03	16.68 ± 0.45
P9	37.2 ± 1.64	7.90 ± 0.005	42.88 ± 0.01	91.23 ± 0.55	-5.23 ± 0.11	15.73 ± 1.02
P10	41.6 ± 1.67	12.56 ± 0.02	43.6 ± 0.02	90.4 ± 1.07	-5.19 ± 0.15	16.74 ± 1.32

[12], being immersed in water for 8 hours, gently buffered with filter paper in order to remove the excess water and then dried for 24 hours at 110°C in a hot air oven; the water solubility (WS) value was calculated with (6) relation:

$$WS, (\%) = (W_0 - W_f)/W_0 * 100 \qquad (4),$$

where W_0/W_f represents the initial/immersed and dried mass of film, (g). [1]

All determinations were performed in triplicate.

RESULTS AND DISCUSSION

Physical Properties

All film samples showed low adhesion to the drying surface, being easily removed from the silicone support, flexible, without breaking, allowing bending and having a pleasant and uniform appearance when valued with the naked eye. They did not taste or smell, and the color is noted in Table 1. Decrease in brightness of samples with higher amounts of agar (P2, P3,

P8) and sodium alginate (P6, P10) and increase in samples with high amount of starch (P4, P5, P9) can be noticed. The sample colors were yellow of different intensity, as it can be seen at a*, b* values from CieLAB determination (Table 1). The hue intensity of the agar or sodium alginate films is due to the raw material whose color is darker. The film thickness varied from 29.4 μm to 41.6 μm, being lower for the samples with higher amount of agar into composition (P2, P3 – 2g agar), and proportionally higher as the sodium alginate mass was added.

P4 and P5 assay (2g of starch into composition) showed close values – 30 and 30.6 μm. P7, the sample of interest due to its completely hydrosolubility (Fig. 3) presents an intermediate value of thickness, but high brightness and intermediate value of color parameters a* and b*.

The Film Solubility. Peleg model

The results are shown in Table 2. The k_1 constant values decreased with the increase in temperature, highlighting the fact that the water transfer increases as the temperature increases.

The same trend was reported in studies of other food rehydration [11], [14]–[17] The k_2 values increase as temperature increases, excepting the P1, P6, and P10 samples.

The water absorption capacity increases with temperature, when k_2 decreases with temperature; it depends on the type of the material, its structure, and also on the chemical composition. [11]

The lower the k_2 value is, the greater the water absorption capacity is (in this case P1, P6, P10, not taking into account P7 sample, which has completely solubilized).

The results indicate that the higher the temperature value, the higher the moisture content of the product. Both situations of decreasing k_2 values with temperature have been reported for wheat and sorghum, as well as their growth for lupine and roasted lupine. [15]

R^2 values over 0.99 (with few exceptions) confirm the possibility of using this model to describe the kinetics of water absorption in a certain temperature range.

Rehydration Ratio (RR)

At 20°C, rehydration ratio values of the films tested were into the range 3.32-27.7. (Fig.1)

High values were obtained for P8, P9, P10 samples due to their low moisture content (see Table 1); the highest values were obtained for sample P8, and the lowest ones for P3.

P3 sample, obtained from 2g agar and 1g of starch, maintained the minimum rehydration ratio, for both temperatures, and the sample P8, obtained from 1.5g agar, 1g of starch and 1g of sodium alginate, retained the highest value.

Regarding the increasing temperature at 40°C, the lowest value of RR was found at sample P3 (3.7) and the highest –at P8 (27.7) (Fig 2). An increase in the RR value is observed with the increase in temperature. The low RR values are due to the low hydrophilicity and the inability to soak a high volume of water, leaving the pores unburied, thus damaging the structure during dehydration process. [16]

Water solubility is a measure of water absorption capacity, being an important indicator of material water resistance. Except for P7, the films

Table 2: Peleg model k_1, k_2 constant values.

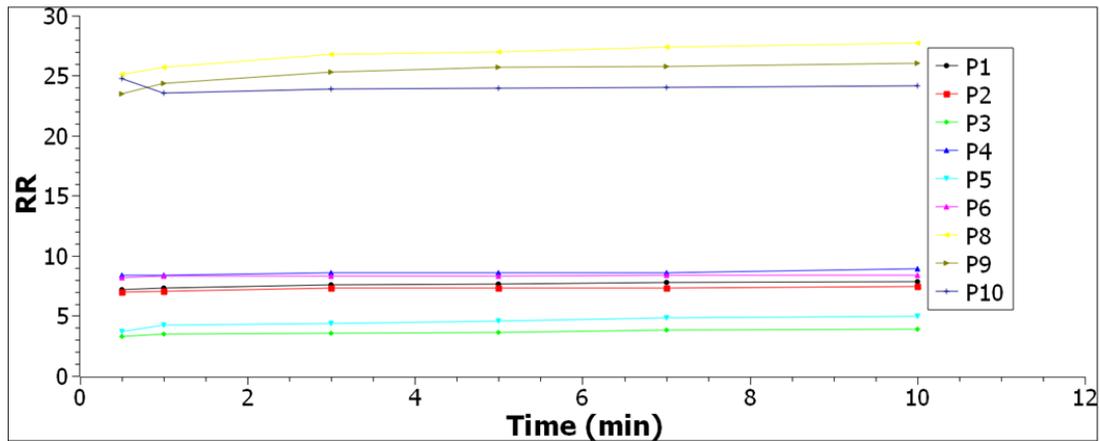| Assay	20ºC			40ºC		
	k_1 x 10^{-3}/ min %$^{-1}$	k_2/%$^{-1}$	R^2	k_1 x 10^{-3}/ min %$^{-1}$	k_2/%$^{-1}$	R^2
P1	2.7	78.94	0.997	1.3	77.52	0.998
P2	0.2	80.86	0.999	0	83.33	1
P3	1.1	44.11	0.973	5.6	48.54	0.998
P4	0.2	80	0.999	0	81.39	1
P5	1.8	53.43	0.987	0.8	53.76	0.991
P6	0.2	83.33	0.999	1.5	82.19	0.998
P7	complete solubilization			complete solubilization		
P8	0.2	89.74	0.999	0	89.28	1
P9	0.4	87.72	0.999	0.36	87.21	0.999
P10	2.7	88.23	0.999	0.17	89.28	0.999

Fig. 1: The effect of 20°C temperature on rehydration ratio.

have retained their integrity, although they have changed their consistency.

The highest water solubility was reported at P7 sample (film with high sodium alginate content), and the lowest one at P3 sample (without sodium alginate). It can be concluded that the addition and the increase of sodium alginate amount increase the water solubility, as well as the behavior at P7 sample, obtained from 2g of sodium alginate (the highest amount) and 1g of starch.

As can be seen from the obtained data, the film with the highest amount of agar into composition showed

poor solubility, and high hidrophobicity, respectively.

Therefore, we can conclude that materials can be obtained with ingredients such as starch or sodium alginate, so as to get completely hydro soluble packaging, while we can use agar into the composition of moisture-resistant packaging material.

The determination of swelling ratio index is an important parameter when used as a food packaging material, especially if it has high moisture content or it has been stored in relatively humid environments. P7 sample could not be tested because it lasted only 3 minutes in water at 20°C.
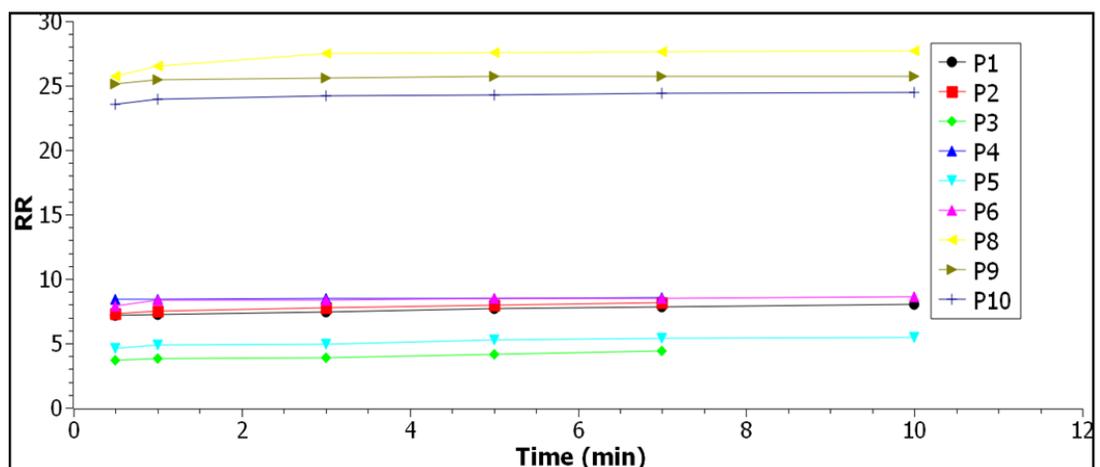

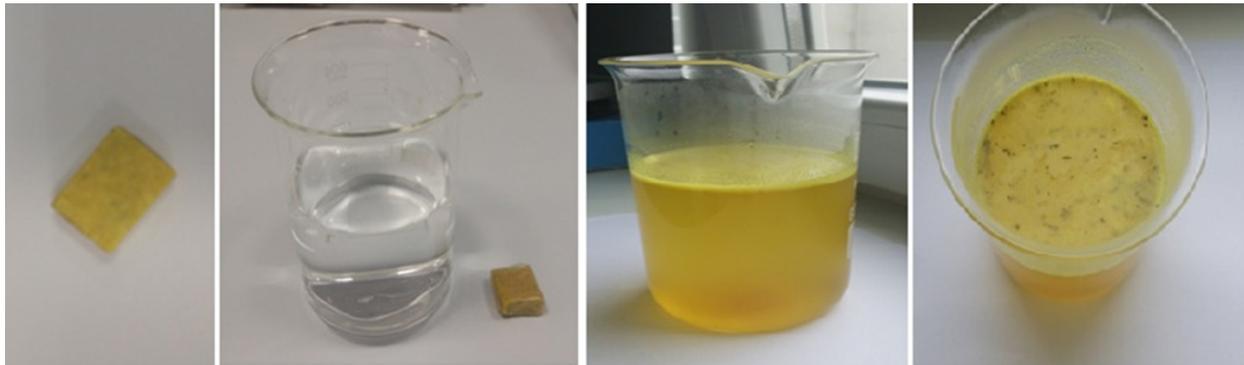*Fig. 2: The effect of 40°C temperature on the rehydration ratio.*

Fig. 3: Full solubility of P7 sample after maintenance 20 seconds at temperature over 80°C.

The lowest absorption and swelling ratio capacity were identified in P3 and P5 samples, those with high amount of agar and starch into the composition (sodium alginate low content) (Fig 4).

The data confirm the strong hydrophilic nature of sodium alginate and the hidrophobicity of agar and starch.

In order to determinate traces of metals in the film, all samples were tested and the obtained results confirm their safe human consumption, from this point of view (values below the detection limit for As, Pd, Ag, Te, Hg, Pt, Pb).

CONCLUSIONS

In order to obtain a completely hydrosoluble packaging material, the ideal recipe is based on 2g alginate, 1g starch and 1g glycerol. Determinations, such as swelling ratio, water solubility, moisture content, and rehydration ratio, provide the information needed in order to establish the destination of edible packaging material. Their completely solubility in a short time successfully qualifies them for producing packing materials for instant drinks, spices, flavors, dyes, or other powdered products.
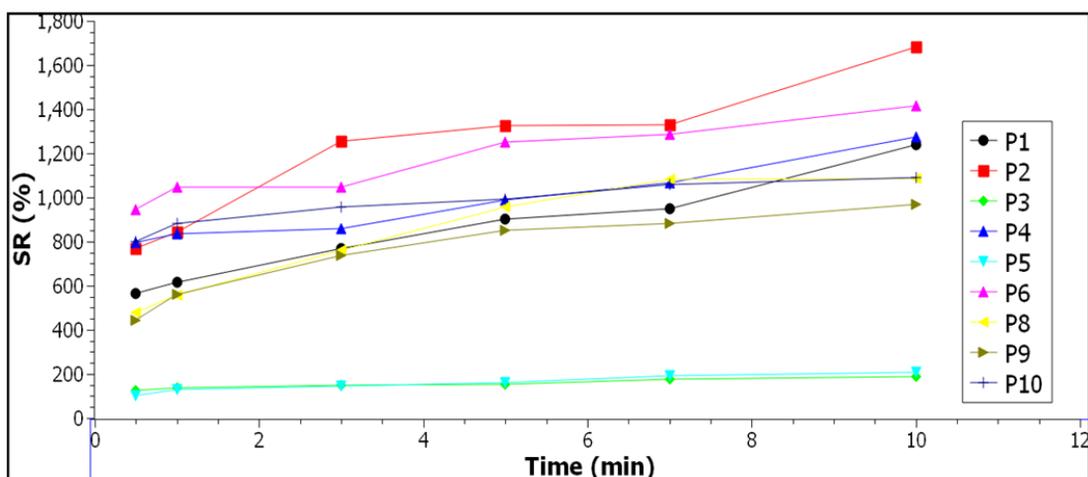

Fig. 4: Swelling ratio index for the tested films.

REFERENCES

[1] Kanmani, P., Rhim, JW. (2014). "Antimicrobial and physical-mechanical properties of agar-based films incorporated with grapefruit seed extract". *Carbohydrate Polymers* 102: 708-716, doi: 10.1016/j.carbpol.2013.10.099.

[2] Othman, S.H. (2014). "Bio-nanocomposite materials for food packaging applications: types of biopolymers and nano-sized filler". *Agriculture and Agricultural Science Procedia* 2: 296-303.

[3] Siah, W.M., Aminah, A., Ishak, A. (2015). "Edible films form seaweed (*Kappaphycusalvarezii*)". *International Food Research Journal* 22(6): 2230-2236.

[4] Sousa, A.M.M., Souza, H.K.S., Liu, L., Goncalves, M.P., (2015). "Alternative plasticizers for the production of thermo-compressed agar films". *International Journal of Biological Macromolecules* 76: 138-145; doi: 10.1016/j.ijbiomac.2015.02.030.

[5] Abreu, A.S., Oliveira, M., de Sa, A., Rodriguez, R.M., Cerqueira, M.A., Vicente, A.A., Machado, A.V., (2015). "Antimicrobial nanostructured starch based films for packaging". *Carbohydrate Polymers* 129: 127-134.

[6] Tavassoli-Kafrani, E., Shekarchizadeh, H., Masoudpour-Behadabi, M., (2016). "Development of edible films and coatings from alginates and acrrageenans. Review." *Carbohydrate Polymers* 137: 360-374.

[7] Mali, S., Sakanaka, L.S., Yamashita, F., Grossmann, M.V.E., (2005). "Water sorption and mechanical properties of cassava starch films and relation to plasticizing effect". *Carbohydrate Polymers* 60: 283-289, doi:10.1016/j.carbpol.2005.01.003.

[8] Turhan, M., Sayar, S., Gunasekaran, S., (2002). "Application of Peleg model to study water absorption in chickpea during soaking". *Journal of Food Engineering* 53: 153-159.

[9] Gutium, O., 2014. "Hidratare a boabelor de năutdupămodelul Peleg" in *Papers of the Sibiu Alma Mater University Conference*, Eight Edition, 2:120-124.

[10] Peleg, M., 1988. "An empirical model for the description of moisture sorption curves". *Journal of Food Science* 53(4): 1217-1219.

[11] SalimiHizaji, A., Maghsoudlou, Y., Jafari, S.M., (2010). "Application of Peleg model to study effect of water temperature and storage time to rehydration kinetics of air dried potato cubes". *Latin American Applied Research* 40: 131-136.

[12] Rhim, JW, Park, HM, Ha, CS (2013). "Bio-nanocomposites for food packaging applications". *Progress in Polymer Science*, 38:1629-1652. doi: 10.1016/j.progpolymsci.2013.05.008.

[13] Wang, LF, Rhim, JW (2015). "Preparation and application og agar/alginate/collagen ternary blend functional food packaging films". *International Journal of Biological Macromolecules*, 80:460-468.

[14]   Pavelkic, V. *et al*., (2015). "Application of Peleg model on mass transfer kinetics during osmotic dehydratation of pear cubes in sucrose solution". *Chem. Ind. Chem. Eng.* Q 21(4):485-492, doi 10.2298/ CICEQ141014004P.

[15]   Sadik, J.A., Demelash, B., Gizaw, M., (2013). "Hydration kinetics of teff grain". *Agric. Eng. Int.* 15(1): 124-130.

[16]   Kashiri, M., Kashaninejad, M., Aghajani, N., (2010). "Modelling water absorbtion of sorghum during soaking". *Latin American Applied Research* 40: 383-388.

[17]   Krokida, M.K., Marinos-Kouris, D., (2003). "Rehydration kinetics of dehydrated products". *Journal of Food Engineering* 57(1): 1-7.