Controlled Foaming of Cereal Protein Foams

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ABSTRACT

A foam model based on a prolamin protein (zein) and starch from maize has been developed. A mathematical model for the foam density was developed which elucidated the relationship between the ingredients, the process parameters and the foam properties.

INTRODUCTION

Foamed materials are currently used in different fields and applications: from packaging to insulation, and in food and biomaterials. Besides the physical and chemical properties of the materials, cell structure is crucial, different cells size lead to different insulation and mechanical properties and even to different texture. Thus, these properties could be modified by varying the percentages of the main ingredients and process parameters such as the foaming temperature, in other words by controlling the foaming process.

This work was focused on a cereal foam made of the protein zein, maize starch, plasticizer and foaming agent. The materials were first mixed together, in the right proportions, with distillate water to form a melt and then introduced into a hot mould (two parallel, heat controlled plates) were the foaming process took place. This foam model was developed and characterized in order to investigate how the materials and process parameters affected the foam properties. A mathematical model able to predict the foam density was developed based on measurements on both melt and foam.

Specific measurements were performed on two different mix, identified by the model in having equal density but quite different structure.

MATERIALS AND METHODS

Materials and foam development

Zein (Moisture content, MC = 4.9% wet basis), and corn starch (MC = 11.8% wet basis), was purchased from Sigma-Aldrich (Stockholm, Sweden). Citrofol A1 (triethylcitrate, min. 99%) was from Jungbunzlauer (Ladenburg, Germany) and baking powder (ammonium carbonate E503) was produced by Santa Maria (Mölndal, Sweden). The moisture content of zein and starch was determined by drying over night in an oven at 110 ºC.

Distilled water was added to the correct amount of these powder (see the following paragraphs) and a dough was formed using a 10g mixer (ReoMixer^{TM}, Reomix Instruments, Lund, Sweden). Moreover, the total amount of flour was set to 10g and the quantity of zein and starch was expressed in relation to the flour content. The temperature of this process was set at 40ºC, above the glass transition temperature of the zein, and kept constant by a water bath connected to the mixing beaker. The mixing was performed until the registered torque reached 9 Nm since the stiffness of the dough would have otherwise compromised the safety of the reomixer. This means that different recipes were mixed for different times to allow the same development of the protein network inside the dough.

The foaming process was performed by baking. The dough was heated inside a hot mould, consisting of two parallel, heat controlled plates, for 40 minutes and to obtain a product with a disc shape, thick enough to notice the foam structure. An aluminium frame of 20 mm thickness and with a hole of 50 mm diameters was used, see Fig. 1, to consent a perfect bubble growing.

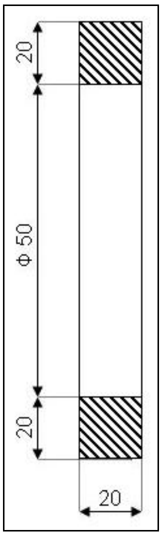

Figure 1. Section of the frame used; unit mm.

Model foam structure and development

Through screening experiments the process was tested and an average recipe was found (5g of zein, 5g of starch, 0,3g of baking powder, 0,75g of citrofol A1 and 6,5g of distilled water) and four different factors identified. The factors were recognized as the amount of zein/starch, of plasticizer, of foaming agent and the mould temperature; besides, due to other trials, their limiting values were determined as:

Zein: [40%; 60%]. Because with a lower amount of zein the final product couldn’t be considered foam, while with a higher one it was a shell.

Plasticizer (Citrofol A1): [0.5g; 1g]. Because was not possible, with a lower amount, obtaining a dough, instead, with a higher one, in the bottom of the mixing beaker remained a little water and a little plasticizer as well.

Foaming agent (baking powder): [0g; 0.6g]. Since achieving a dough was not possible with more foaming agent.

Mould temperature: [120ºC; 200ºC]. Since at lower temperature the final product was still wet and collapsed during the storage and since at higher temperature the product began burning.

All the other possible factors, e.g. the mixing time and temperature and the baking time, were kept constant. The final recipe and the process parameters are listed in Table. 1.

Table 1. List of final recipe and the process parameters.

INGREDIENT/PROCESS PARAMETER	VALUE
Zein	[40%; 60%]
Plasticizer	[0,5g; 1g]
Foaming agent	[0g; 0,6g]
Water	6,5g
Mixing temperature	40 ºC
Mixing time	Until the mixing torque reaches 9 Nm
Baking temperature	[120 ºC; 200 ºC]
Baking time	40’

Since the different recipes used polymers with a density (ρ_p) that could be considered constant, foam density (ρ_f) was preferred to relative density (R), see Eq. 1, and it was chosen as response.

$$R=\rho_f/\rho_p \quad (1)$$

Volume and weight were measured after two days storage at constant temperature and humidity, respectively 23 ºC and 50%.

As suggested by Sleeper[1], the model development was divided into two phases. In the first one the system was assumed linear and this hypothesis was tested by the addition of centre points. In case of non-linear behaviour, phase two, a three level treatment structure would have been chosen with the addition of few more runs to the previous ones. Thus, in phase one, it was chosen a full factorial treatment structure characterized by 16 corner points and 4 centre points and one replication, and, since there was evidence of a non-linear behaviour, it was changed into a three levels face centred central composite design. For this reason, 10 further run, corresponding to 2 centre points and 8 axial points, were added. The program used to generate the completely randomized design structure and to realize the model was Design Expert 7.1.6. (Science Plus Group, Groningen, Nederland). In order to verify the model 3 trials were made.

Foam characterization

After two days storage at 23 ºC and 50% R.H., three different samples per recipe were cut twice (perpendicularly to the main axis) in a randomized way. Thus six pictures per recipe were scanned with a Canon CanoScan N1240U scanner (Canon Inc., Tokyo, Japan) and analyzed due to AnalySIS (Soft Imaging System).

A sequence of filters and actions (in order DCE, the color separation of green, binarizition and the morphological filter of erosion) was used to fix the images to the further analysis. A grid with a detection of 15 pixel^2 was used to obtain all the data about the cells geometry; with the exception of the area and the orientation, all the other average parameters values (sphericity, convexity, aspect ratio and diameter maximum) were weighted average values, where the weight was the area of the cell itself. The mean volume-weighted star volume and the surface density, were estimated with Eq. 2 and Eq. 3, as explained by Reed and Horward[2] and by Weibel R. Ewald[3], respectively.

$$\bar{v}_V^* = \frac{\pi}{3} \cdot \bar{l}_0^3 \qquad (2)$$

Where $\bar{l}_0^3$ was the average of the cubed lengths of the chords detected.

$$S_{Va} = 2\frac{I_a}{L_c} \qquad (3)$$

Where I_a was the number of intercepts and L_c the total length of the chords detected. To measure the mean volume-weighted star volume (Eq. 2) and the surface density (Eq. 3) the distance between the chord spacing was set as 20 pixels, and each image was rotated four times of 90 º each.

Dough measurements

The flow curves of doughs were characterized by applying the Cox/Merz rule in their own LVE regions for oscillatory tests. The consistency index and the power-law index were determined. Hyperbolic Contraction Flow[4] tests were used to predict the foaming properties of the dough by the extensional viscosity and the strain hardening index.

These measurements were performed in an Instron Universal Materials Testing Machine model 5542 (Canton, USA), The nozzle had an inlet radius (r_0) of 10 mm, an outlet radius (r_1) of 3 mm, and a height (H) of 15 mm. The test was performed at 40 ºC at four different extension rates: 0.1, 0.5, 1 and 2 s^{-1} in a randomized order.

RESULTS AND DISCUSSION

The program ran the ANOVA on the three level structure and gave the results presented in Table 2.

Table 2. Summary of the ANOVA results.

	p-value	
Source	Prob > F	
Model	< 0.0001	Significant
A-percentage zein	< 0.0001	
C-foaming agent	< 0.0001	
D-temperature	0.2367	
AC	0.0019	
AD	0.0008	
C^2	< 0.0001	
Residual		
Lack of Fit	0.0417	Significant
R-Squared	0.91	
Adj R-Squared	0.89	

The model had an F-value of 40.59 which implied it was significant, there's only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Moreover values of "Prob> F" less than 0.5% indicated which model terms were significant; thus A (percentage of zein), C (amount of foaming agent), D (temperature) and the other factors AC, AD and C^2 were significant. Only the p-value of temperature indicated that it was not significant by itself, but since hierarchy is a condition *sine qua non*, and since the factors AD was significant the temperature was significant as well. In addition the R-Squared value of 0.91 and the Adjusted R-Squared value of 0.89 showed that the model fitted the reality quite well. The only bad aspect was the "Lack of fit F-value" of 5.00. Nevertheless, the number of replication used, 1 instead of 3 or more as the good practice would have suggested, and further analysis on the residuals led to think of the presence of outliers. For this reason the model, represented in coded factors in Table 3, was accepted as valid.

Table 3. Final equation in terms of coded factors.

Density	=
+0.285167	
-0.04489	* A
-0.02961	* C
+0.004889	* D
+0.014938	* A * C
-0.01644	* A * D
+0.038333	* C^2

Two recipes, identified by the model in having equal density but quite different structure (Fig. 2), were the objects of the foam characterization.

The first one was: 40% zein, 0.5g of plasticizer, 0.6g of foaming agent, 6.5 g of distilled water and 120 ºC was the mould temperature.

The second one was: 60% zein, 0.5g of plasticizer, 0g of foaming agent, 6.5 g of distilled water and 120 ºC was the mould temperature.

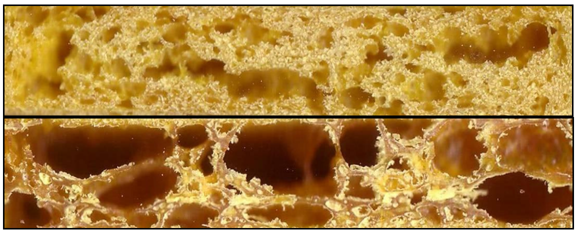

Figure 2. Section sample of the two different foams having equal density: 40%zein (top) and 60%zein (bottom).

In Table 4 are presented the main interesting values detected with the image analysis.

Table 4. Results from Image Analysis.

	Area [mm^2]	Volume weighted star volume [mm^3]	Surface density
40% zein	0.55±0.14	1.89±1.32	3.36±0.48
60% zein	3.55±0.67	29.46±14.35	1.57±0.07

Comparing the results form the image analysis, the main difference between the two different recipes was represented by the area of the single cell; the 40% zein foam had 0.55 mm^2 whereas the 60% zein had a value at least 6 times bigger. Results from stereology (Table 3) led to the conclusion that foam characterized by 40% zein had cells with isotropic shape while the 60% zein foam did not. This was confirmed by the quite low value the surface density of the 60% zein foam: a cell with such a big value of volume weighted star volume would have had a higher value of surface density if would have been isotropic.

According to the Fig. 3, both doughs showed a tension-thinning behavior and in particular the 60% zein had higher value of extensional viscosity.

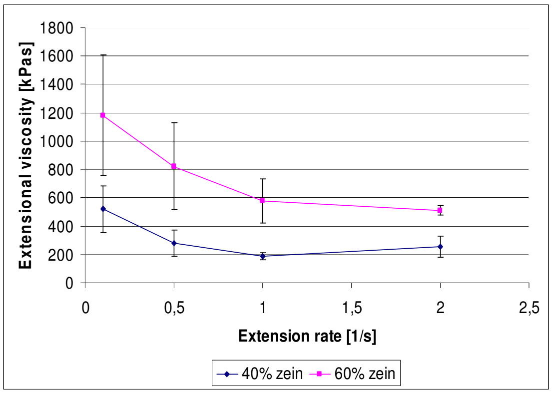

Figure 3.Extensional viscosity of the doughs.

Table 5 shows that both doughs showed were strain hardening for extension rates higher than 0.1 s^{-1} and increasing with increasing extension rate. The comparison between those two series of data led to say that the amount of zein is connected to the strain hardening effect, the more zein the higher strain hardening index; meaning that zein had the ability to form entanglements.

Table 5. Strain hardening index (p=0.05, n=3).

Extension rate	0.1 [s^{-1}]	0.5 [s^{-1}]	1 [s^{-1}]	2 [s^{-1}]
40% zein	0.98 ± 0.27	1.27 ± 0.03	1.27 ± 0.10	1.50 ± 0.34
60% zein	0.99 ± 0.30	1.42 ± 0.49	1.40 ± 0.43	1.74 ± 0.41

The fact that the foam with worse cells characteristic (isotropy and cells average area) was originated by dough with better foaming properties (extensional viscosity and strain hardening) lead to think that another cause affected the foaming process. This could be identified with the swelling of the starch; during mixing the starch granules absorbed water and inside the hot mould they started gelatinization and swelling until the foam was totally dried. Obviously the rate of this process was related to the baking temperature; while the starch was swelling the cells had the possibility to grow.

In Fig. 4 this effect is evident, in particular for 40% zein foams: the higher the temperature, the faster the drying of the foam and the higher the density.

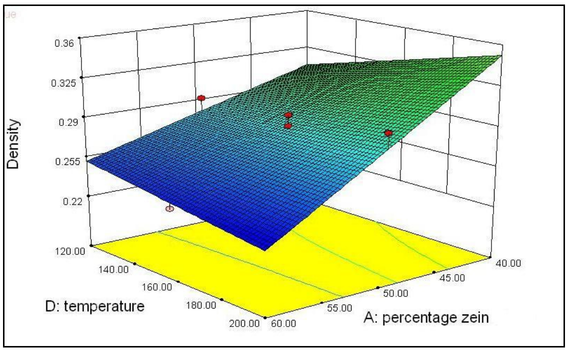

Figure 4. Relation between the amount of zein/starch (A) and the mould temperature (D) in terms of density.

This phenomenon seemed to have less importance for dough of 50% zein where the effect of the temperature related to amount of starch was almost not influent, while for 60% zein recipes higher mould temperature led to a lower density. One possible cause of this behavior could be represented by the rate of water vaporization that in this case behaved like a foaming agent. According to the model the main factors, involved in the foaming process, were the amount of zein and foaming agent, while plasticizer had no influence even if it was necessary to form dough; in particular the more zein and foaming agent the lower value of density.

The presence of foaming agent had relevance in what was related to the density and thus the foam characteristics, according to the amount of zein. In particular: with a low amount of zein (40%) the foaming agent had a fundamental importance in terms of porosity (the more foaming agent the more numerous the cells), while in 60% zein foams its effect was mitigated by the presence of the other foaming agent, the water. In other words, in 40% zein dough, during the foaming process, the foaming agent had the power to create cells expanding walls, while the water vaporization did not; instead in the 60% zein their effects were summed. The result of this sum was anyway not visible since the dough, at the foaming temperature, was not able to retain gas bubbles as well as the 40% zein dough where the swelling process of the starch was significant.

CONCLUSIONS

The foam model was widely analyzed by measurements on both dough and foam. To elucidate the foaming properties of the protein melt and how foams are influenced by the ingredients and their amount. Moreover, a mathematical model regarding the foam density was developed and verified.

ACKNOWLEDGMENTS

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