Journal homepage: http://fens.usv.ro/index.php/FENS
Journal of Faculty of Food Engineering,
Ştefan cel Mare University of Suceava, Romania
Volume XX, Issue 3 - 2021, pag. 172 - 181

INFLUENCE OF THE COMBINATION OF EMULSIFIERS ON THE PROPERTIES OF RICE GLUTEN-FREE DOUGH AND THE QUALITY OF BREAD

***Iryna MEDVID [1], Olena SHYDLOVSKA [1], Tetiana ISHCHENKO[1]**
[1]*Department of Hotel-Restaurant Busines, National University of Food Technologies, Volodymyrska str. 68, Kyiv, 01601, Ukraine,* medvidrina@gmail.com,
*Corresponding author
Received 31th March 2021, accepted13th September 2021

Abstract: *The article investigates the influence of low-fat lecithin, sunflower oil, and dry egg white on the rheological properties and microstructure of gluten-free rice dough and quality indicators of ready-made bread. To determine the effectiveness of the use of these emulsifiers, the bread technology with implementation of enzyme modificated (by amylolytic enzymes) flour starch was used. To assess the rheological state of the dough, its viscoplastic properties (shear stress and effective viscosity of the test systems) were analyzed using a rotary viscometer. The dough microstructure was examined by microscopy. Traditional methods to determine physical and chemical indicators of ready-made bread quality were used. The results showed that the emulsifiers implementation changed the behavior of rice dough, and had the positive effect on the qualitative (specific volume and porosity). It has been found that the use of a combination of emulsifiers from low-fat lecithin, sunflower oil, and dried egg white in rice bread technology in combination with enzymatic modification of flour starch significantly improves the rheological properties and structure of gluten-free dough and provides high indicators of specific volume and porosity of ready-made products.*

Keywords: *gluten-free bread, rice dough, sunflower oil, lecithin, dried egg white.*

1. Introduction

The priority task of the food and restaurant industries in today's conditions is to expand the sector of production of products for special dietary consumption [1], intended for the treatment and prevention of food-borne diseases. One of the common ones is celiac disease, which occurs in 1-3 % of the world's population [1, 2]. It's the immune-mediated reaction to gluten of genetically predisposed people [3], which is accompanied by damage and inflammation of the small intestinal mucosa and malabsorption of many important nutrients such as iron, folic acid, fat-soluble vitamins, calcium [4, 5]. Despite the progress in the understanding of the pathogenesis of celiac disease and the development of new therapy methods, nowadays, only the strict gluten-free lifetime diet is the safest and the most effective method of patients' treatment, which means constant removal of gluten from the diet [1, 3]. Generally, the term "gluten" combines the prolamins of some cereals that contain specific toxic oligopeptide sequences – wheat gliadin, rye secalin, and barley hordein [4]. The increasing incidence of celiac disease is leading to an increase in demand for gluten-free foods [3], so the development of new technologies is an extremely important issue.
The preparation of gluten-free bread is a complicated technological task, as

DOI: https://doi.org/10.4316/fens.2021.019

prolamins play a key role in ensuring the unique structural and mechanical properties of the dough [1, 6, 7]. As a basis for the production of non-gliadin bread, rice flour is becoming increasingly popular. This raw material is a source of vegetable protein, complete in amino acid composition, contains sodium, potassium, phosphorus, magnesium, vitamins B1, B2, and PP, a high amount of easily digestible carbohydrates, has a mild taste and white color [8, 9]. However, gluten absence in the rice flour leads to the preparation of dough, which has reduced structural and mechanical properties, dense porosity of the crumb of the ready-made product, and other quality defects [10].

The analysis of existing scientific research shows that to improve the quality of gluten-free bread made of rice flour, the use of ingredients, imitating functional properties of gluten was suggested by many scientists [7, 11]. To this end, it is important to include in the formulation of hydrocolloids (gums of plant origin, microbial polysaccharides, cellulose and its derivatives, modified starch) [2, 3, 12-14], proteolytic enzymes and transglutaminase [8, 15], emulsifiers (DATEM, sodium stearoyl lactylate, lecithin) [9], raw materials with high protein content (isolates and concentrates) [16] and combinations.

To prevent the loss of carbon dioxide bubbles formed during dough fermentation and their coalescence, the use of lecithins as structural agents is promising, which not only act as emulsifiers but are also a valuable source of phospholipids that are important physiologically [17]. The molecule of lecithin is hydrophilic (polar) on the one hand and hydrophobic (non-polar) on the other, which improves the efficiency of its use in combination with fats of vegetable, animal origin or shortening [4]. This leads to better plasticization of gluten-free bread, reduction of adhesion, and, consequently, sticking of the dough to the working parts of equipment and its losses during the bread production.

Taking into consideration the fact, that patients with celiac disease typically have low protein intake, it is promising to model the viscoelastic behavior of gluten in the dough and improve the texture of the final product by using raw materials high in protein, which also improves the nutritional value of products [3]. The functional ingredient with a structure-forming effect is dry egg white, the properties of which can be considered as a display of three molecular aspects: hydration, emulsifying, and hydrodynamic (rheological) properties [18].

Rice flour is characterized by a high content of starch (75-81 %), a small amount of mono-, disaccharides (0.6-0.7 %), which are essential for the yeast metabolism and activity during fermentation, and low activity of its own α- and β-amylases. Due to this, rice flour is a potential raw material for modifying its carbohydrate composition using amylolytic enzymes, the substrate of which is starch. In order to enrich the dough with sugars, we selected α-amylase of fungal origin and glucoamylase, the joint use of which catalyzes the hydrolytic decomposition of glucoside bonds of starch molecules with the formation of maltose, glucose, and dextrins of different molecular weights. According to the results of previous studies, it was determined that the use of enzymatic modification of rice flour starch in the preparation of the dough contributes to a more intense course of microbiological processes, which is displayed in the activation of gas and acid accumulation [19].

Since research on improving the properties of dough and the quality of gluten-free bread remains a topical issue, the aim of this article was to analyze the effect of a combination of lecithin emulsifiers, sunflower oil, and dried egg white on rheological properties, and microstructure of rice dough using an enzymatic modification of flour starch with the help of fungal α-amylase and glucoamylase and quality indicators of ready-made products.

2. Matherials and methods

2.1. Raw matherials

The rice flour (8 g/100 g of protein, 80.3 g/100 g of starch, 0.7 g/100 g mono- and disaccharides and humidity 11.5 %) produced by “Cascade” LLC, Ukraine; pressed baker's yeast (Lesaffre, Ukraine); salt (Artemsil, Ukraine) and tap one water were used in the preparation of gluten-free bread.

Hydrolysis of rice flour starch was performed using amylolytic enzymes: fungal α-amylase Alphamalt VC 5000 SN (Muhlenchemie, Germany) with an activity of 5000 SKB/g, the optimal operating conditions of which pH 4.7, temperature 37-40 ºC; glucoamylase Glucomil (Germany), the activity of which is 500 AMG/g, optimal pH 3.0-5.5, temperature 40-64 ºC. The citric acid (Mriya, Ukraine) was also used in the studies.

Low-fat sunflower lecithin (Dniprotechnologies Research and Production Center, Ukraine) with a phospholipid content insoluble in acetone, 96.5 %, was used as a structuring ingredient; refined sunflower oil (Sandrade, Ukraine); dry egg white (Ovostar Union, Ukraine) with a mass fraction of protein substances of 85 % and a solubility of 93.7 %.

2.2. Methods

Enzymatic modification of rice flour starch

Since the temperature and acid optimums of fungal α-amylase and glucoamylase differ, the modification of the carbohydrate composition of rice flour was performed at a temperature of 40 ºC and pH 4.7, which are optimal for both enzymes. In order to maintain the appropriate pH of the environment, citric acid was used in an amount of 0.065 % by weight of flour. α-amylase (0.005 % by weight of flour) and glucoamylase (0.03 % by weight of flour) were pre-dissolved in the water at a temperature of 25-30 ºC at hydro module 10. To carry out the enzymatic modification, a mixture of 50 % of rice flour from its prescription amount, citric acid, enzymes, and water was hydrolyzed in an electric thermostat at 40 °C for 120 min until the accumulation of sugars in it 5.9 %. The humidity of the flour mixture was 65 % [19].

The dough making and bread baking

The following dosages of ingredients (g per 100 g of rice flour) were used during the preparation of the dough: low-fat sunflower lecithin (1 g), refined sunflower oil (3 g), dry egg white (4 g), compressed yeast (3 g) and salt. (1.2 g).

After fermentation, lecithin, oil, and dry egg white were added to the obtained hydrolyzate from rice flour, dispersing it for 5-7 min at a rotational speed of the working body of the food processor (Electrolux, Sweden) of 100-120 min^{-1}. To prepare the dough with a humidity of 53 %, a modification of the steamless method was used. Yeast suspension, salt solution and the second part of rice flour according to the recipe were added to the rice flour hydrolyzate with the structure-forming ingredients dispersed therein. The dough was kneaded on a food processor with replaceable nozzles (Electrolux, Sweden) for 8-10 min. Then the dough pieces were formed by hand and subjected to fermentation in steel molds for baking in a stand (UNOX, Italy) for 50 min at a temperature of 30-32 °C and a relative humidity of 75-80 %. Baking was performed at a temperature of 180 °C in a humidified baking cabinet (UNOX, Italy) during 25-30 min. The ready-made bread weighing 400-450 g was cooled for 180 min.

To compare the effect of amylolytic enzymes and structure-forming ingredients (using their concentrations mentioned above) on the properties of gluten-free dough and the quality of rice flour bread, 4 samples of test systems were prepared: control (without additives); with enzymes; with enzymes, lecithin and oil; with enzymes, lecithin, oil and dry egg white.

Rheological (viscous-plastic) properties of gluten-free dough

Rheological properties of the dough after kneading and after 50 min of fermentation were determined at a temperature of 25 °C on a rotary viscometer "Reotest-2" (Germany), which is equipped with replaceable cylinders with different diameters: external – S and internal – S_2. Samples of the semi-finished product with a moisture content of 70 % weighing 20-25 g were placed in the measuring system of the device and read α at 12 shear rates in mode A, each of which corresponds to a shear deformation constant or shear rate D_r (s^{-1}): 1a – 1; 2a – 1.8; 3a – 3; 4a – 5.4; 5a – 9; 6a – 16.2; 7a – 27; 8a – 48.6; 9a – 81; 10a – 145.8; 11a – 243; 12a – 437.4. The increase in the shear rate occurs when the speed of rotation of the inner measuring cylinder by switching the gearbox.

The shear stress (τ, Pa) was calculated using the instrument scale readings (α) and the constant of the inner cylinder (z), which for S_2 is 5.91 Pa according to the following equation:

$$\tau = z \times \alpha \quad (1)$$

When calculating the effective viscosity (η, Pa*s), the data of shear stress (τ, Pa) and shear rate (D_r, s^{-1}) were taken into account. Equation [20] was used to determine this indicator:

$$\eta = \frac{\tau}{D_r} \times 100 \quad (2)$$

Based on the obtained results, viscosity curves (dependence of viscosity on shear stress) η = f(τ) were constructed.

To characterize the change in the effective viscosity of the dough systems during maturation, the degree of dilution (K, %) was determined by the following equation:

$$K = \left(1 - \frac{\eta_{\text{after kneading the dough}}}{\eta_{\text{at the end of dough fermentation}}}\right) \times 100 \quad (3)$$

Gluten-free dough microstructure

Studies of the microstructure of gluten-free rice dough were performed using an electronic scanning microscope JSM-6060 LA (JEOL, Japan), equipped with an energy dispersion spectrometer Oxford X MAX-80T. After 50 min of fermentation, the test specimens were frozen, dried under vacuum, subjected to fracture, sprayed with ash on the fracture area of 5 mm. After that, they were examined at a magnification of 1000 times and the most expressive areas were photographed.

Physical and chemical quality indicators of gluten-free bread

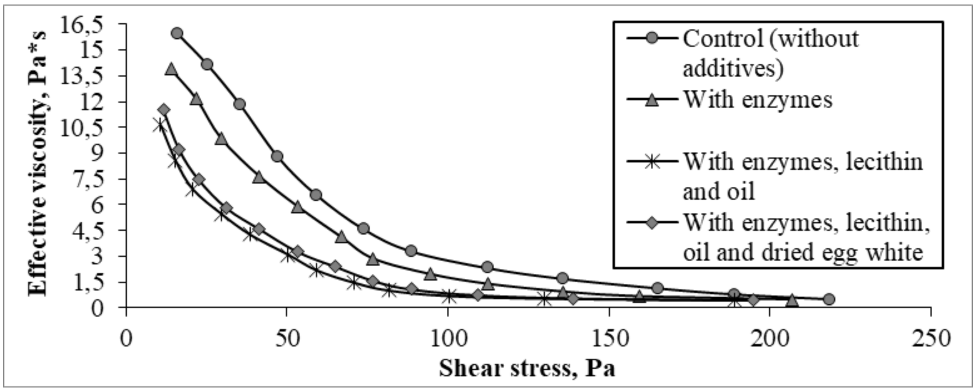
The determination was performed not earlier than 3 hours after baking of all samples. The specific volume of bread was calculated as the ratio of the volume it occupies to its weight (cm^3/g).

Porosity of the finished products was determined at a Zhuravlev device in line with a known procedure [19]. The results of experimental studies were statistically processed using the standard Microsoft Office software package.

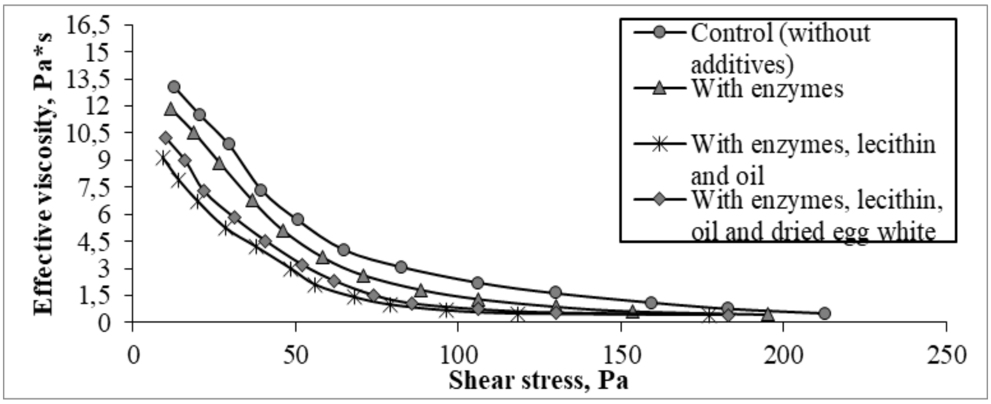
3. Results and discussion

3.1 Characteristics of the rheological properties of gluten-free dough

Rheological properties of gluten-free dough are decisive in the formation of qualitative characteristics of finished bakery products. Their adjustment allows to influence such indicators of bread quality as specific volume and porosity, which in general characterizes the consumer value of products. Information on the influence of ingredients used in rice bread technology on the rheological behavior of the dough is given by the analysis of viscoplastic properties of dough systems after kneading (a) and after 50 min of fermentation (b) on a rotary viscometer Reotest-2 (*Figure 1*).



a)



b)

Fig. 1. Rheological viscosity curves
(a) after kneading and (b) at the end of dough fermentation

It was determined that right after kneading the dough *(Fig. 1, a)* the value of the effective viscosity for the samples using the enzymatic modification of rice starch decreases in comparison to the control. It's explained by dehydrating properties of mono- and disaccharides formed during the hydrolytic decomposition of starch under the action of α-amylase and glucoamylase. Additional application of low-fat lecithin together with sunflower oil reduced the viscosity of the dough system with enzymes compared to the sample without emulsifier. This was facilitated by the ability of the oil, adsorbed on the surface of starch grains and protein micelles, to prevent swelling of these colloids and increase the content of the liquid phase of the dough. The introduction of dry egg white into the dough causes an increase in its effective viscosity in relation to the sample with enzymes, lecithin and oil, which is probably the result of the interaction of the protein matrix of flour with the active groups of animal protein molecules. Analyzing the rheological viscosity curves at the end of the dough fermentation *(Fig. 1, b)*, it was found that the effective viscosity of all test samples decreases due to the hydrolysis of dough biopolymers. However, determining the degree of dilution (K, %) of test systems *(Table 1)* indicates a slowdown in the relaxation of their structure during maturation.

Table 1

The degree of dilution of the dough systems during the maturation period

Name of the sample	**Effective viscosity, Pa*s**		**The degree of dilution (K, %)**
	η after kneading the dough	**η at the end of dough fermentation**	
Control (without additives)	15.96	13.00	23.0
With enzymes	13.89	11.82	18.0
With enzymes, lecithin and oil	10.64	9.16	16.0
With enzymes, lecithin, oil and dried egg white	11.53	10.22	12.8

It was found that the use of enzymatic modification of flour starch in rice bread technology reduced the degree of dough thinning by 21.7 % compared to the control, and additional application of lecithin with sunflower oil – by 30.4 %. The results can be explained by the deepening of colloidal processes in the dough, which are probably related to the ability of dextrins formed due to the action of α-amylase on starch, to bind a significant amount of free moisture; partial complexation of surfactants with flour components, as well as high activity of unsaturated fatty acids of vegetable oil in the formation of complexes with proteins and starch polysaccharides.

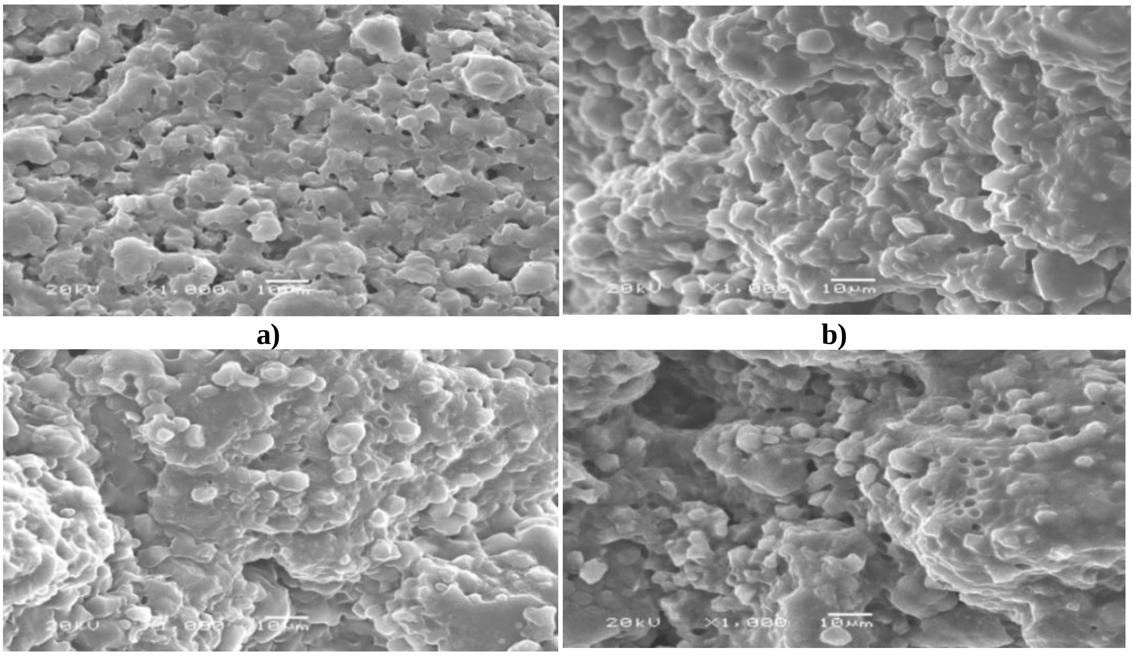
The use of dry egg white as a structuring agent in combination with enzymes, lecithin and oil reduced the degree of dilution of the dough by 1.7 times compared to the control, from which we can conclude that the use of a combination of these ingredients increased the structural viscosity of gluten-free rice dough, i. e. improving its rheological properties.

3.2 Gluten-free dough microstructure

During dough preparation, flour biopolymers undergo significant structural and conformational changes, which are accompanied by swelling, peptization, and enzymatic cleavage of the components [21].

A more thorough explanation of the effect of amylolytic enzymes, lecithin, oil and dry egg white on the structural and mechanical properties of gluten-free rice dough can be obtained by microscopy (*Figure 2*).

Analysis of the obtained microphotographs showed that samples of rice dough with used enzyme modificated flour starch *(Fig. 2, b, c, d)* were characterized by the presence of smaller grains of starch compared to the control, on their surface in some places spots similar to deepening are visible, which is probably due to the hydrolytic action of α-amylase and glucoamylase. The more continuous structure of the studied dough samples than the control can be explained by the better intensity of microbiological processes during maturation, as well as the interaction of incomplete products of hydrolysis of starch – dextrins, with moisture and other components of the dough system.



a) **b)** **c)** **d)**

Fig. 2. The microstructure of the dough:
a – *control (without additives),* **b** – *with enzymes,* **c** – *with enzymes, lecithin and oil,*
d – *with enzymes, lecithin, oil and dry egg white*

The dough microstructure with lecithin and oil in combination with amylolytic enzymes *(Fig. 2, c)* was more homogeneous and monolithic in comparison to samples without emulsifier and fat, which can be explained by wrapping of starch and its hydrolysis products with fat pellicle and possible formation of complexes with molecules. The results from the study of the dough microstructure with additional introduction of dry egg white *(Fig. 2, d)* indicated that its colloidal solution promoted the adhesion of starch grains and other components in the dough system, forming conglomerate protein-polysaccharide complexes, which creates a more developed dough structure during the fermentation period.

Thus, the results of studies of the rheological properties and microstructure of gluten-free rice dough with the studied structuring agents indicate an improvement in its structure, which will improve the quality of ready-made products, in particular the specific volume and porosity.

3.3 The research of physical and chemical indicators of gluten-free bread quality

Important criteria for assessing the impact of raw ingredients on the quality of finished products are the specific volume and porosity of the bread, which reflects the ratio of pore volume to total crumb volume. The digestibility of bread is also related to the amount of porosity [20]. The results of the study of these physical and chemical quality indicators for gluten-free rice bread using amylolytic enzymes, lecithin, oil and dry egg white in its technology are presented in *Table 2*.

Table 2

Physical and chemical quality indicators of gluten-free bread

Quality indicators	Gluten-free rice bread samples			
	Control (without additives)	With enzymes	With enzymes, lecithin and oil	With enzymes, lecithin, oil and dried egg white
Specific volume, cm^3/g	1.31	1.51	1.97	2.53
Change in control, %	-	*+15.3*	*+50.4*	*+93.1*
Porosity, %	36.7	41.4	51.5	65.5
Change in control, %	-	*+12.8*	*+40.3*	*+78.3*

It was found that the most pronounced effect on the specific volume and porosity of the ready-made products has a joint use in their technology of lecithin, oil and dried egg white in combination with the modification of rice flour starch with amylolytic enzymes. Thus, the use of a combination of these structuring ingredients increased the specific volume of bread by 93.1 %, while the porosity of the crumb was improved by 78.3 % in comparison to the control sample. So, the analysis of the results of the quality of rice bread samples confirms the patterns obtained during the study of the rheological properties and of the dough microstructure.

4. Conclusion

According to the results of the research, the expediency of modifying the carbohydrate composition of rice flour with the help of amylolytic enzymes and the joint use of low-fat lecithin, sunflower oil and dried egg white as structure-forming ingredients in the technology of gluten-free bread. Their positive effect on the rheological properties and microstructure of the dough was determined. Particularly, the decrease of the effective viscosity and the degree of dilution of the dough systems with the introduction of the suggested components in relation to the control without additives, which can be noted as an improving effect. Due to the lower viscosity of the dough, the carbon dioxide bubbles that are the part of the dispersed phase expand more while baking, and the ready-made products are characterized by higher values of specific volume and porosity. Ensuring the required quality of rice bread using enzymes, lecithin with oil and dry egg white is also due to a significant improvement in the structural and mechanical properties of the dough examined by microscopy.Taking into consideration the high efficiency of these structuring ingredients in combination with enzymatic modification of flour starch to improve the properties of the dough and quality indicators of ready-made products, bread technology with their use can be implemented in the baking industry and in the production conditions of restaurants.

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