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THE EFFECT OF USE OF GUAR GUM WITH PECTIN MIXTURE IN GLUTEN-FREE BREAD

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ABSTRACT

The quality of gluten-free bread, obtained by using pectin, guar gum and their 1:1 mixture was compared. Basing on the distribution of carbohydrate fractions present in crumb extracts, acquired using size exclusion chromatography, the trial to explain differences in interactions between these hydrocolloids and corn starch was made.

Key words: gluten-free bread, food hydrocolloids, bread aging, retrogradation, crumb texture

INTRODUCTION

Bread - one of the most basic food products - has shown to be harmful for a group of people including those with celiac disease. This gluten-sensitive enteropathy is triggered by dietary gluten, and treatment of the patient with a gluten-free diet leads to its remission [32, 33].

To obtain good results gluten must be removed from all eaten food products [9, 27] including bread. The removal of this important structural component is only possible if we replace it with other water binding compounds- hydrocolloids. In gluten-free bread production the most commonly used are pectin, guar gum, xanthan gum and locust bean gum [11, 34, 2, 23].

In Poland, the most widespread water binding substance used in gluten-free bread production is highly methylated pectin [2, 24]. However, ready to eat bakery products available in the market reveal poor taste and flavour, and their crumb is crispy and quickly hardens [27].

The aim of this research was to introduce a new recipe for gluten-free bread, which would replace pectin with other hydrocolloid improving organoleptic properties of the product and extending shelf time, at comparable costs. The attempt to explain the different interactions between used hydrocolloids and corn starch, used in gluten-free bread baking, was undertaken.

MATERIALS AND METHODS

The ingredients and recipes for gluten-free bread baking are shown in [table 1](#). They were based on many previous experiments [7]. Laboratory bread baking was performed using straight procedure, which consisted of the following stages:

1. Mixing of dough ingredients to obtain uniform consistency (approx. 10 min.)
2. Putting balanced dough portions (250 g) into baking pans
3. Fermentation for about 40 min. at 40°C.

Table 1. Recipes of the dough used for baking gluten-free bread

No	Bread type	Potato starch [g]	Corn starch [g]	Corn flour [g]	Pectin [g]	Guar gum [g]	Yeast [g]	Sugar [g]	Salt [g]	Oil [cm ³]	L-lisyne [g]	L-threonine [g]	Water [g]
I	Pectin-standard	100	400	-	25	-	25	30	8	-	0.23	0.23	510
II	Guar	120	480	-	-	21.6	30	36	10.5	18	0.23	0.23	680
III	Pectin-guar	120	432	48	10.53	10.53	30	36	10.5	18	0.23	0.23	680

The loaves were baked in oven VIVA Meteor type MD 08/6511 at 230°C for half an hour. Four loaves were obtained basing on each recipe. After 1.5 hours of cooling, they were balanced, then oven loss and bread efficiency were calculated [13].

The volume was measured in grainy material, using rape seeds. The loaves not selected for analysis on the day of baking were stored in packages (used in bakery for packing) at 23-24°C and 64% relative moisture content. Then, they were analysed after 24, 48 and 72 hours after baking.

Sensoric assessment was conducted on the day of baking, according to PN-89/ A-74108. The bread quality class was established basing on overall score.

To study bread aging, the following parameters were measured every day during the whole storage period:

1. Moisture content, according to PN-89/ A-74108, by drying approx. 1 g of crumb from the inner part of loaf.
2. Texture profile, using texture analyser TX-XTA with XTR1 software. A loaf was torn into halves, from each part the slice of 3 cm thickness was taken, on both slices texture profiles were measured, from which hardness, gumminess, chewiness and resilience were calculated.
3. Apparent amylose content in water extracts of crumb. To this end, 10 g of crumb was extracted using the procedure of Neukom and Rutz [22], the obtained product was clarified with Carrez I and Carrez II solutions and fullfilled with water to 100 cm³. After filtering, blue value was measured as described by Morrison and Laignelet [21] at wavelength 635 nm using Specord M-42 (Karl-Zeiss Jena) spectrometer. Blue value is defined as extinction of 10 mg iodine stained starch dissolved in 100 cm³ of water. It's calculated from the formula:

$$Bv = E \cdot 10 \text{mg/dry_mass}$$

where: E - extinction.

As dry mass total carbohydrate content, established by anthrone method [20] was taken.

To explain the reasons of different interactions between used hydrocolloids and corn starch, size exclusion chromatography of the extract was conducted, as described by Gambuś [6].

Analysis of the obtained fractions included:

- total carbohydrate assessment with anthrone method [20]
- iodine-staining at 640 and 525 nm [28],

pullulan standards were used for molecular weight calibration.

RESULTS AND DISCUSSION

[Table 2](#) contains the results concerning the influence of used hydrocolloids and recipe on baking indices and quality of gluten-free bread. Bread, in which gluten was replaced by highly methylated pectin, was taken as a standard. Such mixtures are commonly available for persons with celiac disease.

Table 2. Influence of hydrocolloid and recipe used on baking factors and quality of gluten-free breads; I - III description of recipes - see table 1

Recipe	Weight of cold bread [g]	Total baking loss [%]	Yield of bread [%]	Moisture of crumb [%]	Scores	Grade
I	214.0	14.5	168	51.3	32	II
II	217.5	13.0	175	54.8	35	II
III	220.3	11.9	177	53.7	37	I

Loaves, which contained guar gum or its mixture with pectin at 1:1 ratio, revealed higher mass of cold bread, and so lower oven loss in comparison to standard bread. Their crumb had

higher water content, then in case of pectin-only bread, probably due to better swelling of guar gum, which lead to holding of larger part of water in crumb during baking.

Loaves with guar gum had the highest volume- they were 9% bigger than those with mixture of guar gum and pectin and 12% as compared to pectin-only bread (fig. 1). However, they were qualified to II class of organoleptic quality, due to large, unregular pores in crumb. The same quality class was given to pectin bread, because of crumb crispiness (table 2). The similar results have been already described [6, 1]. Sensory results proper for I quality class were only found in case of bread with mixture of guar gum and pectin.

Fig 1. Impact of hydrocolloid selection on bread volume

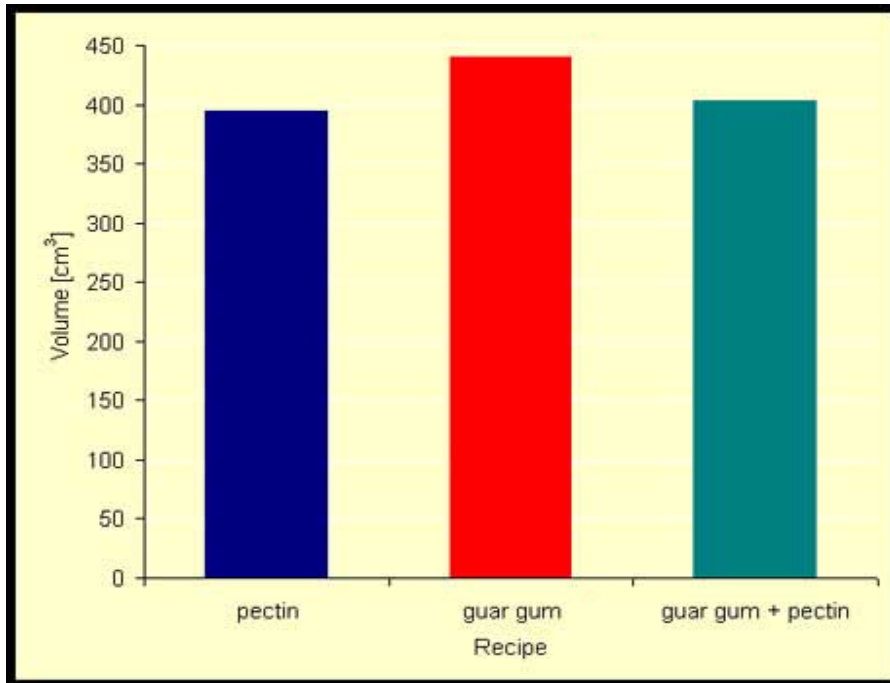
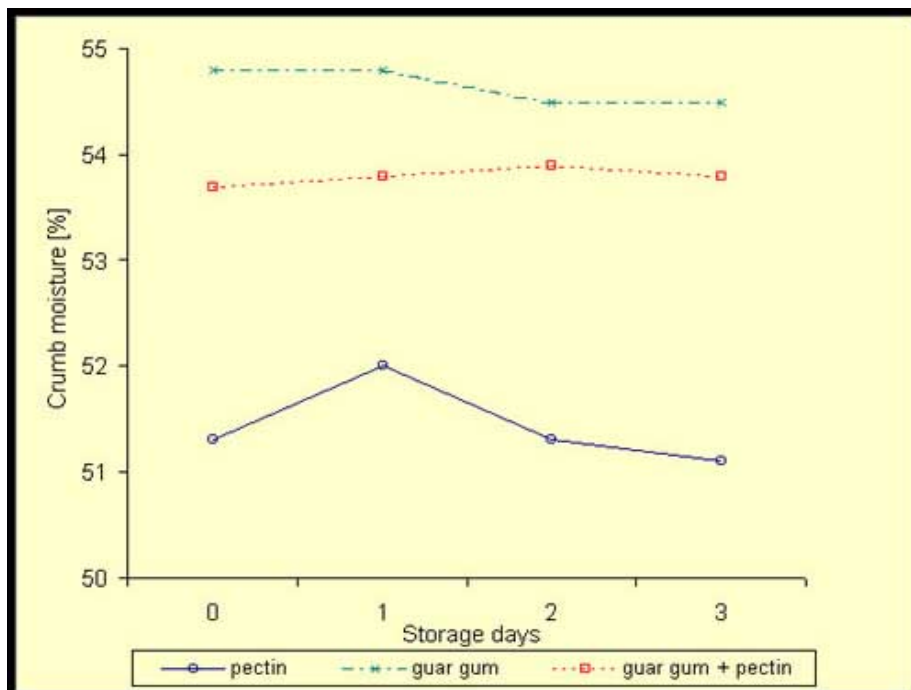


Fig 2. Crumb moisture changes during storage of gluten-free breads



Texture profile analysis has shown, that on the day of baking, the best crumb parameters, ie. the lowest hardness (fig. 3), the lowest chewiness (fig. 5), and the highest resilience (fig. 6) are characteristic for bread with guar gum. The gumminess of all studied loaves on the day of baking was the same (fig. 4).

Fig 3. Crumb hardness changes during storage of gluten-free breads

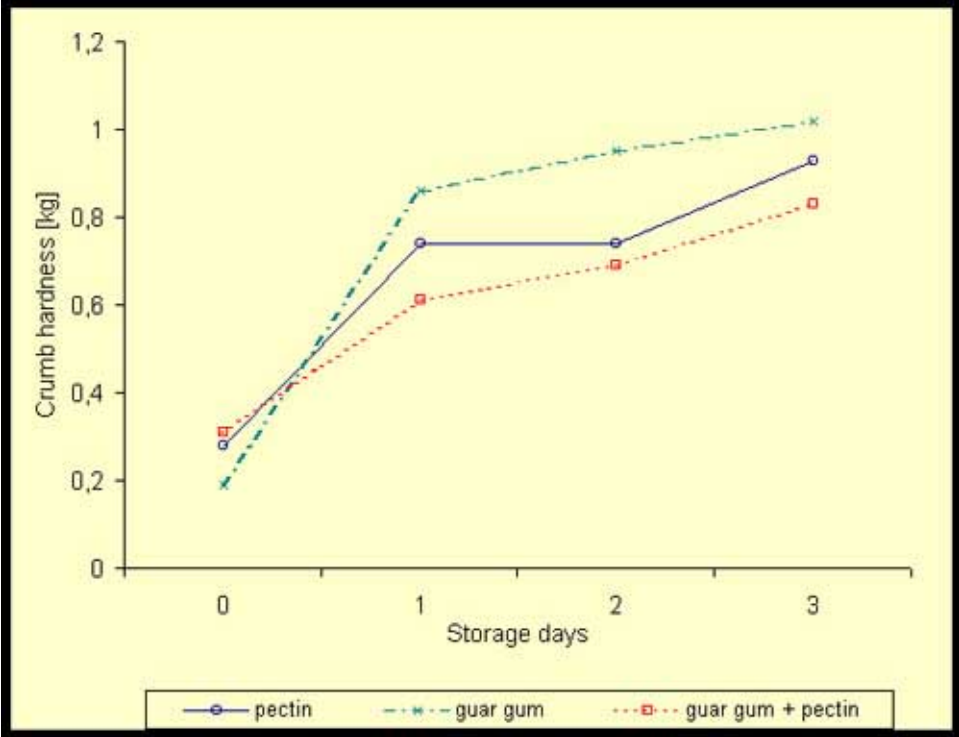


Fig 4. Crumb gumminess changes during storage of gluten-free breads

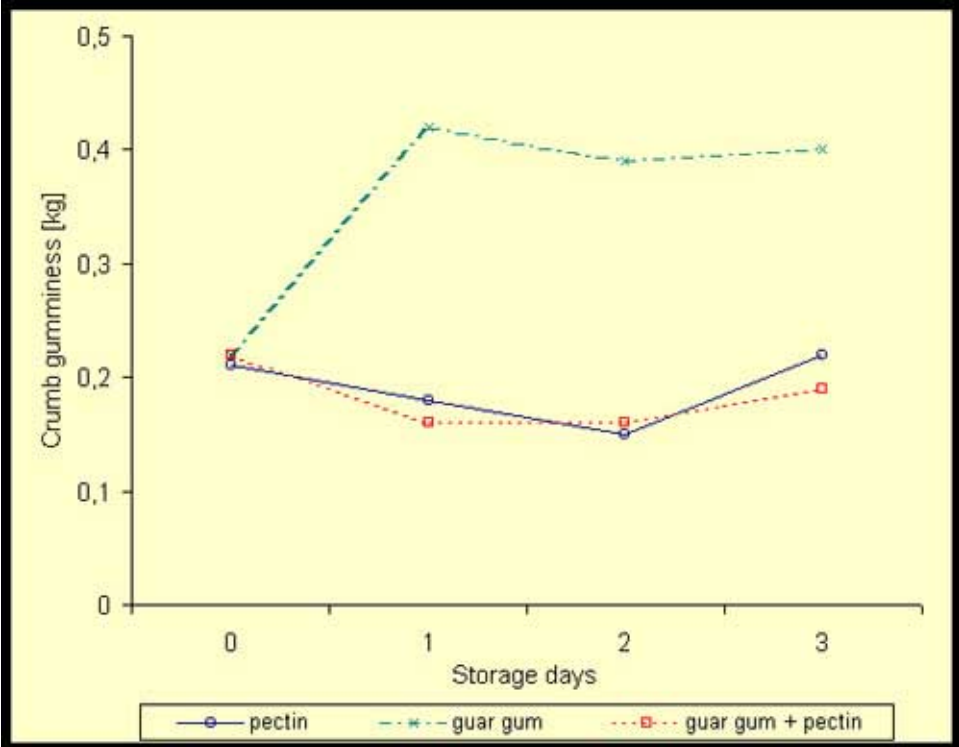


Fig 5. Crumb chewiness changes during storage of gluten-free breads

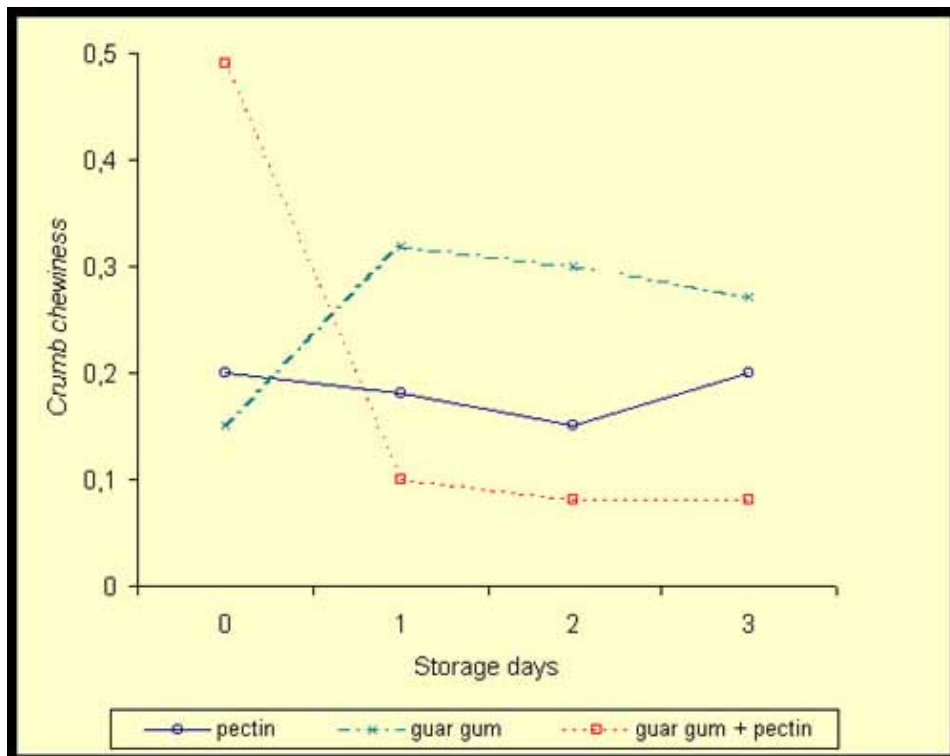
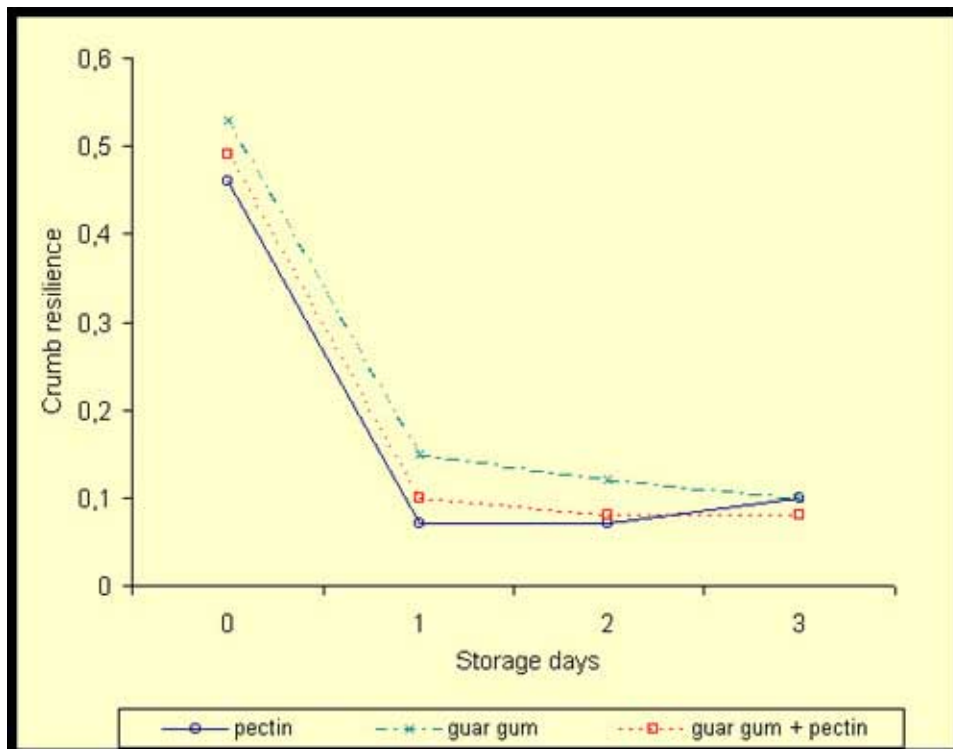


Fig 6. Crumb resilience changes during storage of gluten-free breads



Further studies concerned aging process of the obtained loaves. To this end, they were stored at stable conditions, at room temperature for 3 following days and on each day moisture content and texture profile of its crumb were checked.

As it's shown on [fig. 2](#), during storage in all cases little loss of moisture content in crumb could be observed, which is in agreement with literature [14, 15, 6]. Standard (pectin) bread revealed the lowest moisture content of crumb during the whole storage time, much lower than the other ones. The lowest moisture changes during 4 days of baking were found for bread prepared with mixture of guar gum and pectin. Probably it influenced the changes of crumb hardness, which were the lowest in comparison to other bread types, and in consequence caused the lowest hardness after 3 days of storage ([fig. 3](#)). Due to very fast hardening of gluten-free bread it seems, that even a little reduction of this process could be regarded as an improvement of its quality [27].

The highest rising of hardness, for all breads, was observed after the first day of storage, similarly to traditional bread types [14, 15, 10, 22]. This change influenced mostly the crumb of bread with guar gum, which significantly lowers the usability of this recipe. Also gumminess and chewiness of this bread after the first day of storage, were unsatisfactory, and this continued to the end of storage time ([fig. 4, 5](#)). However the resilience of this bread remained highest ([fig. 6](#)).

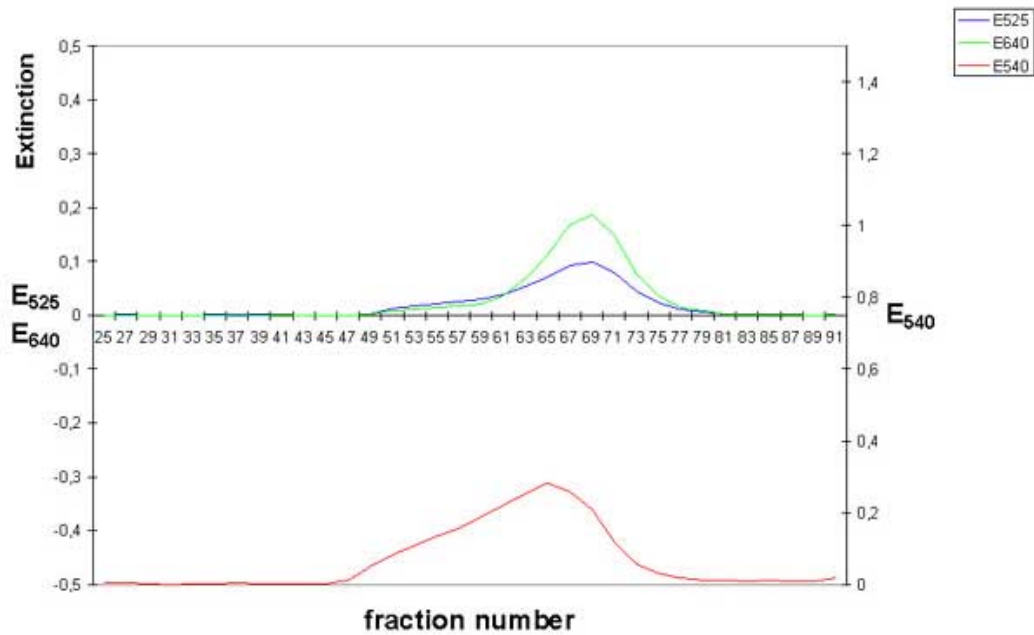
The lowest gumminess and chewiness of crumb after 3 days of storage, was observed in bread with mixture of guar gum and pectin, which proves its better freshness in comparison to bread with only one hydrocolloid ([fig. 4, 5](#)).

Because the above results showed different influence of separate and mixed hydrocolloids on the quality of baked product, the following studies were focused on interactions between starch and hydrocolloids used to bread baking. To this end, water extract of crumb was fractionated on size exclusion system, and measurements of blue value (Bv) as free, unretrograded amylose in crumb were conducted on each day of storage.

It's commonly known that the maximum absorption of iodine-amylose complex is between 640-660 nm and iodine-amylopectin in the range 520-540 nm [3, 4, 31]. Praznik and his co-workers [28, 29, 30] suggest, that the high extinction value at 640 nm, or ratio of extinctions at 640 and 525 nm is enough to prove amylose presence. On the other hand high extinction values at 525 nm and low values of the mentioned above ratio, are indicators of amylopectin. If this is applied to fractions obtained by size exclusion chromatography, one can separate ranges where these glucans are eluted.

The SEC profile of water extract of standard (pectin) bread, prepared on the day of baking is shown on [fig. 7](#). It could be seen, that, on the day of baking, amylose was eluted in fractions 59-77, which corresponds to molecular weights $2-50 \times 10^5$ Da, and fragments of amylopectin in fractions 49-59 ($5-30 \times 10^6$ Da). Total amount of carbohydrates, measured by anthrone method, showed higher amount of amylose (about $162 \mu\text{g}/\text{cm}^3$ of extract, which is about 80% of amylose in crumb) than amylopectin (about $40 \mu\text{g}/\text{cm}^3$ of extract).

Fig 7. Total carbohydrate content and iodine staining of crumb water extract fractions collected from SEC columns on the day of baking of guar bread



In the extract of guar bread crumb (fig. 8), on the day of baking, amylose was identified in fractions 59-73 in much lower amount than in pectin bread extract, but the molecular weight was similar ($4-50 \times 10^5$ Da). Also, much more amylopectin was found in fractions 43-59 ($5-90 \times 10^6$ Da). In total carbohydrate amount, amylose was only 40%, which equaled $51 \mu\text{g}/\text{cm}^3$ of extract, and amylopectin content about $77 \mu\text{g}/\text{cm}^3$ of extract.

Fig 8. Total carbohydrate content and iodine staining of crumb water extract fractions collected from SEC columns on the day of baking of pectin bread

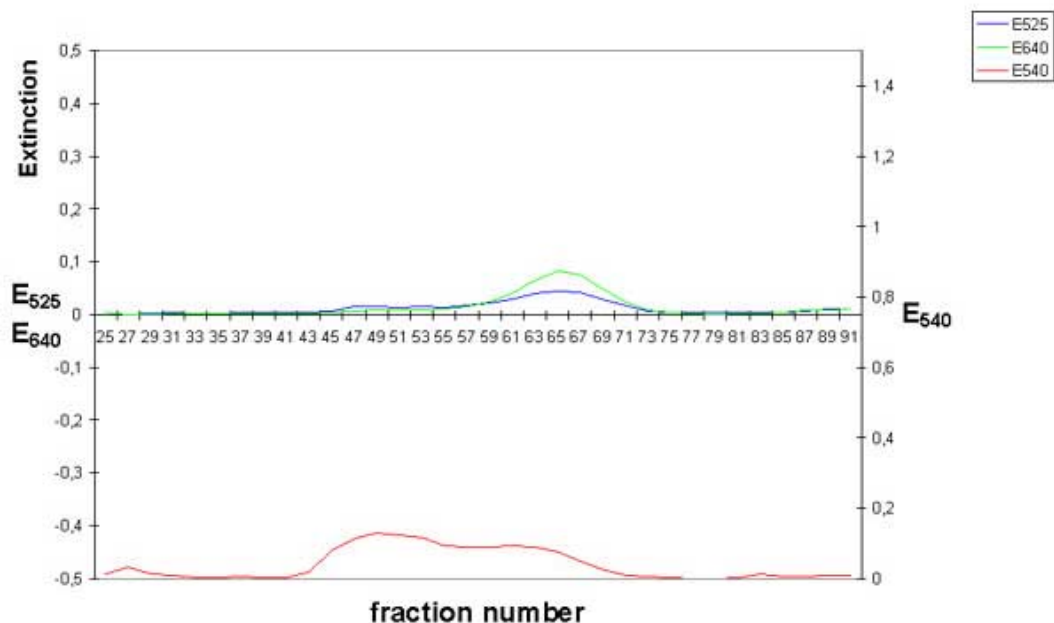
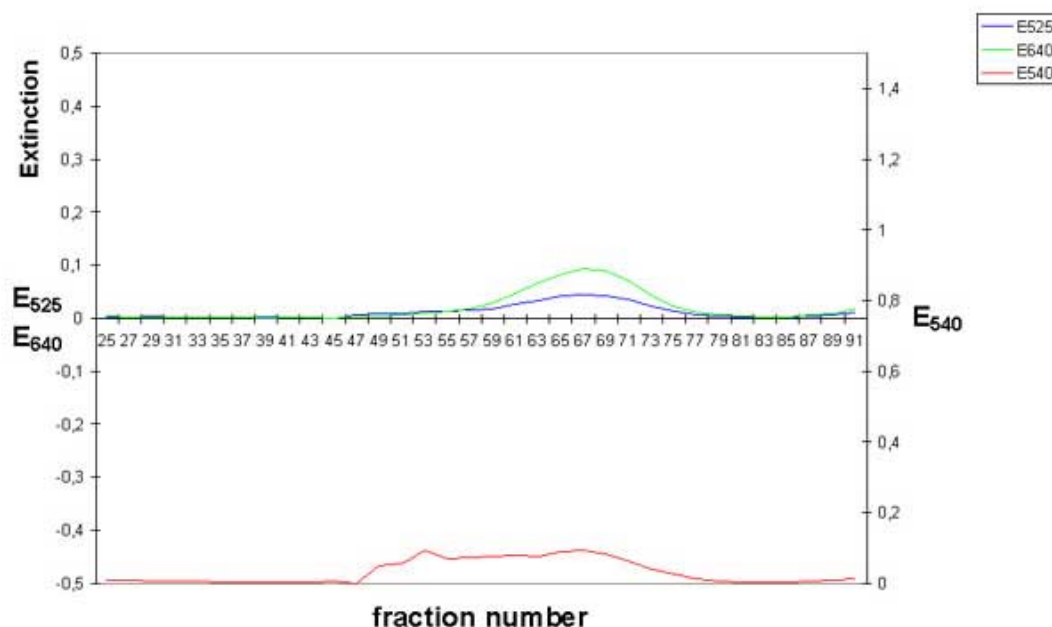


Fig 9. Total carbohydrate content and iodine staining of crumb water extract fractions collected from SEC columns on the day of baking of guar-pectin bread

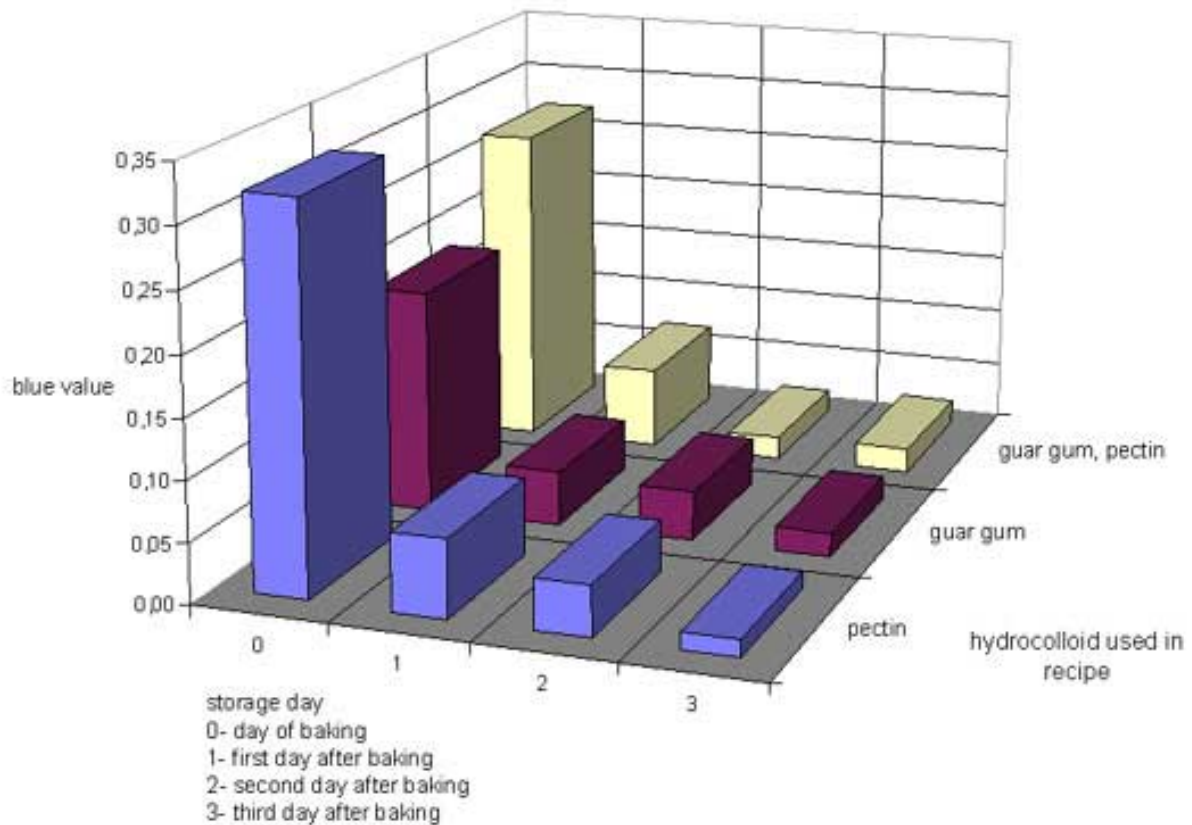


The presence of so large amount of amylopectin signifies high gelatinization of starch in the crumb of bread with guar gum, which is due to high water binding capacity of this hydrocolloid. Water bound during dough formation is freed under baking conditions, and makes easier starch gelatinization [18, 19] and leakage of amylose and in the next step amylopectin. Low amount of amylose in the extract of bread with guar gum should be explained by its high retrogradation, before the extract was prepared, and not by its leakage, which is high. Amylose with short chains could retrograde in the oven or during cooling of loaves after baking [16, 22, 8, 5], because this process is determined mainly by a chain length [25] and high concentration of freed starch linear fraction accelerated its recrystallisation [35].

When the water extract of guar bread's crumb was made, only unretrograded chains of amylose, of size similar to those present in the extract of pectin bread, could be observed. This amylose, in both cases, underwent recrystallisation after the first day of storage ([fig. 10](#)).

Because in the extract of guar bread's crumb, the initial content of amylose was much lower than in the extract of pectin bread, and the rate of retrogradation was close in both cases, it seems, that not the retrogradation of linear fraction, was the main factor of guar bread hardening after the first day of baking. Probably, high extent of starch gelatinization during baking of guar bread was the reason of its fast hardening in comparison to pectin bread ([fig. 3](#)).

Fig 10. Amylose retrogradation in crumb of gluten-free breads, during storage



One of the newest models of bread aging suggested by Martin and Hosney [17], presumes existence of interactions between swollen starch granules and continuous gluten phase (in case of gluten-free bread, thin film of hydrocolloid) in bread, based on relatively weak hydrogen bonds. These bonds during bread aging, when bread loses its kinetic energy, become more numerous and stronger which causes crumb hardening.

Due to the authors of this model, the number of cross-links between starch and gluten (hydrocolloid) is controlled by starch swelling and gelatinisation. When granules are less swollen and less glucans are dissolved, contact area between starch and gluten (hydrocolloid) is limited and weaker cross-links are formed, which reduces hardening. This view was supported by Inagaki and Seib [12], who proved that the more swollen are the starch granules in the bread the more it hardens.

In bread with mixture of guar gum and pectin intermediate amounts of amylose and amylopectin were found (fig. 9). Amylose was eluted in fractions 57-81 which corresponded to $1-70 \times 10^5$ Da, so longer chains were found than in guar bread. Molecular weights of amylopectin, present in fractions 47-57 was significantly lower in comparison to this bread ($7-45 \times 10^6$ Da), which suggests lower gelatinisation of starch granules in the crumb with mixture of hydrocolloids.

Taking into account the content of total carbohydrate fraction, 1 cm^3 of crumb extract contained $100 \mu\text{g}$ of amylose and $39 \mu\text{g}$ of amylopectin. The percentage of amylose in total carbohydrate content was then 72%, and so was higher than in guar bread and slightly lower than in pectin bread ($1 \times 10^5 \text{ Da}$).

However, some short chains of amylose were present in the extract, retrogradation of linear fraction in oven and during cooling was limited by the lower amount of water available under baking conditions, after starch gelatinization [34]. It was bound mostly by hydrocolloids, which have higher water affinity than starch. This could explain high amount of amylose present in bread crumb with mixture of hydrocolloids on the day of baking.

It seems, that the extent of starch gelatinisation in guar bread was lowered by partial replacement of this hydrocolloid by pectin, which positively influenced crumb hardening process of such bread (fig. 3) not lowering its moisture content. It's also likely that, because of no differences in retrogradation rate in crumb of the obtained breads (fig. 10) this limited gelatinization was the reason for longer freshness of such bread.

In breads with pectin and with mixture of guar gum and pectin similar gelatinisation extent was found, which is indicated by almost the same leakage of amylopectin from starch granules - 40 and 39 $\mu\text{g}/\text{cm}^3$ of extract (fig 7. and 9), so changes of crumb hardness were in these cases similar, and differed from guar bread.

CONCLUSIONS

1. Loaves with guar gum revealed better quality in comparison to standard (pectin) bread, because of higher volume, moisture content of crumb, baking efficiency and lower oven loss
2. The use of guar gum and pectin mixture in 1:1 ratio, allowed to eliminate unwanted texture features of bread with only one hydrocolloid, ie. reduce gumminess and chewiness of guar bread and too high crispiness and low resilience of pectin bread.
3. The lowest intensity of hardening was specific for bread with mixture of guar gum with pectin
4. The highest hardening of crumb observed for guar bread during storage was caused not by amylose retrogradation, which was similar in all cases but the highest gelatinisation of starch granules during baking
5. The extent of gelatinisation in bread with guar gum, was reduced by partial replacement of this hydrocolloid by pectin, which positively decreased crumb hardening, not changing its moisture content.

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