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Influence of packaging materials on Kashkaval quality

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Goce Talevski[1], Sonja Srbinovska[2], Dushica Santa[2], Natasha Mateva[3]*

[1]Mlekara AD, Str. Dolnoorizarski pat, 7000 Bitola, Macedonia
[2] Ss Cyril and Methodius University, Faculty of Agricultural sciences and food, Department of animal biotechnology, Blvd. Aleksandar Makedonski bb., 1000 Skopje, Macedonia
[3]Ss Cyril and Methodius University, Institute of Animal Science, Department of Nutrition and Food Products Processing, Blvd. Ilinden 92a, 1000 Skopje, Macedonia

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Abstract

This study focused on investigating the influence of 4 different packaging materials (A - the control, B - polymer emulsion, C - wax and D - polymer foil) on the quality of Kashkaval cheese. The lowest pH value had the sample protected by wax, which is most probably related to the retention of the formed organic acids and gases from the packaging material. A significant influence of the tested packaging materials ($p<0.01$) was found in relation to the content of the dry matter, the proteins and ash, whereas there was no statistical significance in relation to fat content of the Kashkaval cheese. Proteolysis was more intensive samples protected by wax and polymer foil with higher levels of soluble nitrogen, primary and secondary nitrogen products and ripening coefficient compared to the control sample and the polymer emulsion sample.

Key words: Kashkaval, surface treatment, ripening, packaging materials

Introduction

A typical representative of the stretched curd cheeses (*pasta filata*) is Kashkaval, where cheddarization and stretching process of curd at high temperature contributes to its plastic elastic consistency and fiber-like structure. The traditional ripening process of Kashkaval, which implies cheese placement one over another on wooden shelves, is often avoided on industrial scale for several reasons. The main problems associated to that type of ripening are the appearance of mould on the cheese surface, creation of rind, oxidative changes on the surface, weight loss of the cheeses and other diverse effects (Kosikowski and Mistry, 1997).

Coating with paraffin is one of older methods for surface protection of Kashkaval. For that purpose different types of paraffin wax are usually used, which are a combination of the refined food hydrocarbon wax and polymers (Puđa, 2009). Fox et al. (2000) emphasized that certain types of wax used in protection of cheeses can be coloured, whereas certain types of cheeses will be recognized by the consumers (for example: red for Edam, black for extra matured Manchego and Cheddar).

Different types of wax have different melting points, and can influence rheological characteristics, gas penetration from the cheese to the environment or can regulate the moisture and affect that way cheese yield. Çetinkaya et al., (2005) reported significant differences in the sensory characteristics of Turkish cheese Kashar protected with bee wax in different ripening periods.

According to Ebnesajjad (2012), coating the cheese with polymer emulsion (a combination of polyvinyl acetate, plasticizer, colour and certain preservatives) showed to be a good method of

*Corresponding author/Dopisni autor: E-mail: g.talevski@t.mk

protecting the cheese surface. Natamycin (E 235) and sorbic acid (E 200) are the most common used preservatives in polymer emulsion which exert antifungal effect and thus prevent the mould development.

In order to protect the cheese surface from the growth of moulds, polyvinyl acetate (PVA) containing 0.05 % natamycin is usually applied. Reps et al. (2002) showed that PVA with 0.05 % natamycin effectively protected cheese surface against undesirable molds and simplified cheese handling during ripening.

Polymer foils are the mostly used packaging material in cheese production. They inhibit oxygen permeation, therefore gases (CO_2, H_2S) and water formed during the ripening remain in the cheese for longer time, which can influence on the cheese quality (Vujković et al., 2007).

Alternatives for cheese surface protection were studied by different authors. Ozcan et al., (2011) examined the effect of cheese smoking, while Sarikus (2010) analyzed antifungal effects of essential oils mixture consisting of oregano, garlic and rosemary on the rind of the Kashar cheese. Travaglia et al., (2008) followed the effects of the application of maize protein zein on the surface of Gorgonzola cheese and Han (2005) described fungicide characteristics of imazalil etc.

Thus, the aim of this paper is to examine the influence of different packaging materials on the quality of Kashkaval.

Materials and methods

The influence of different packaging materials on the mixed Kashkaval (cow/sheep milk 9:1) produced in Mlekara AD Bitola was examined on 4 variants, as follows:

- Sample A (control - without surface treatment)
- Sample B (polymer emulsion Plasticoat - DSM, Holland)
- Sample C (low temperature wax - Paramelt, Holland)
- Sample D (polymer multilayer shrink bags MLF 40 - Krehalon, Holland)

The production process of Kashkaval is presented in Table 1.

Bulk raw milk was first filtered, then bactofugated and thermallized at 70 °C for 15 sec. After thermization, the milk was cooled to 4 °C and stored in tanks until processing. During cheese production, the milk was heated to 35 °C, following the addition of calcium chloride (Zirax, Russia, 20 g/100 L), coagulating enzyme Maxiren (DSM, Holland) and starter culture TCC 4 (Chr. Hansen, Denmark; *Lactobacillus delbrueckii ssp. bulgaricus* and *Streptococcus thermophilus*). After milk coagulation, the cheese curd was cut, stirred and heated to 42 °C. Subsequently the whey was drained and the curd was pressed for 15-20 min. After pressing, the curd was cut in blocks and left for cheddarization until the required pH level of 5.0-5.2 was reached. The curd was mechanically sliced, stretched and kneaded in hot brine (72-75 °C) with automatic molding machine Modena (Italy). In the next phase, the curd was molded into plastic squares and transferred into chamber for 24 hours at 12-16 °C. After removing the molds, the cheese was immersed into fungicide Natamycin and ripened under controlled conditions at 10-12 °C and 75-85 % relative humidity.

All variants of Kashkaval were protected on the 10th day of production. Analyses of chemical composition (fat, proteins, lactose, dry matter and solids non fat) of the milk used for the production of mixed milk Kashkaval were made by Milcoscan Minor. Freezing point and added water were defined by thermistor cryoscope method (EN ISO, 2009). The specific gravity of milk was determined by a lactodensimeter. Theactive acidity was measured with pH meter Mettler Toledo and titratable acidity was

Table 1. Production process of Kashkaval

Step	Description
1	Bactofugation
2	Thermization (70 °C/15 sec)
3	Cooling (4-6 °C)
4	Coagulation with Maxiren (35 °C)
5	Cutting and mixing the coagulum
6	Heating the curd (42 °C)
7	Pressing and cutting blocks
8	Cheddarization (pH 5.0-5.2)
9	Stretching (72-75 °C)
10	Molding
11	Ripening (10-12 °C/75-85 % RH)
12	Storage (6-8 °C)

determined according to the Soxhlet Henkel method (Carić et al., 2000). The total number of bacteria was measured with Bacto Scan FC, while the number of somatic cells was measured with fluoroptic electronic method - Somascope.

Chemical analyses of the cheese were performed on the 1st, 30th and 90th day of production in five repetitions. The cheese composition was analysed by standard methods as follows dry matter (EN ISO, 2004), fat (EN ISO, 2008), protein, total nitrogen and water soluble nitrogen matters (EN ISO, 2014), ash (Carić et al., 2000) and pH (Mettler Toledo). The ripening coefficient and content of insoluble nitrogen were calculated. Theoretical yields were calculated according to W. Peter (Sabadoš, 1996).

The obtained results were analyzed using ANOVA with STATISTICA (StatSoft version 10). The significance level was set at $p<0.05$ and $p<0.01$. The significance of the difference between the parameter mean values was estimated using the F test.

Results and discussion

Chemical content, physical characteristics and microbiological quality of raw milk used for production of Kashkaval is shown in Table 2.

Content of dry matter (12.57 %), solids non fat (8.62 %) and proteins (3.41 %) significantly affected the yield of Kashkaval.

Milk proteins, which are very important for cheese yield, varied from 3.24 to 3.65 %, and lactose was between 4.28-4.44 %, and was most likely caused by the presence of mastitis in the herds (Havranek and Rupić, 2003).

Added water was quite low amounting about 0.26 % (FP - average -0.523 °C), probably due to the leftovers of cleaning the cooling vats, tanks and pipes, and titratable acidity was in range of 6.6-7.2 °SH. Plants usually use milk with higher acidity for Kashkaval production. According to Kožev (2006) Kashkaval can be produced from milk with 9.2-9.6 °SH acidity but that product is substandard and does not meet quality requirements, therefore it will also have a shorter shelf-life.

Average TBC was 1.307.200/mL and somatic cells count about 607.800/mL which were unsatisfactory results. That is probably related to factors such as unsettled secretion of animals, poor hygiene in primary production, low level of education among farmers etc.

On the first day of ripening, cheese acidity (Figure 1) ranged between 5.13-5.15, but 30 days later pH reached 5.32 (sample C) to 5.40 (sample D)

Table 2. Gross composition and microbiological quality of mixed milk (cow/sheep 9:1) for Kashkaval production (n=5)

Parameter	Min	Max	X	Sd	Cv
Dry matter (%)	12.22	12.95	12.57	0.3123	2.48
Solids non fat (%)	8.37	8.80	8.62	0.2043	2.37
Fat (%)	3.64	4.15	3.95	0.2114	5.35
Protein (%)	3.24	3.65	3.41	0.1641	4.81
Lactose (%)	4.28	4.44	4.37	0.0581	1.32
Freezing point (°C)	-0.510	-0.535	-0.523	0.0093	1.77
Added water (%)	0.00	0.80	0.26	0.3715	142.87
Specific gravity	1.032	1.034	1.033	0.0008	0.08
Active acidity (pH)	6.58	6.75	6.64	0.0653	0.98
Titratable acidity (°SH)	6.60	7.20	6.76	0.2608	3.85
TCB/mL	853000	1855000	1307200	382647.6186	29.27
SCC/mL	389000	890000	607800	205010.2436	33.72

and then on 90th day of ripening it decreased to 5.26 (sample C) and 5.36 (samples B and D). Increasing pH value at the beginning of the cheese ripening according to Kožev (2006) is related to the survival and evolution of LAB after stretching. Also during that 10-12 days long period period, pH value increases are caused by the degradation of proteins and the therefrom resulting larger puffer capacity. Bukau (1993) noted that representatives of *Lactococcus* genus survived the stretching of *Baskija* thanks to synthesis of proteins resistant to thermal shock (Heat Shock proteins, HSPs) which protected them from a physiological shock.

After 30th day slight decrease of active acidity could be noticed due to the presence of residual lactose fermented by LAB active at the ripening temperature from 10-12 °C. These results are similar to the results of several Turkish authors (Tarakci and Kucukoner, 2006; Çetinkaya and Soyutemiz, 2006; Sulejmani and Hayaloglu, 2016) who examined the Turkish kashkaval-type cheese *Kashar*. The lowest pH value (5.26) was detected among wax coated samples with, most probably due to fact that wax does not allow the formed lactic and carbon acid to migrate to the environment. Therefore a secondary absorption in Kashkaval and a decrease of the pH value occur.

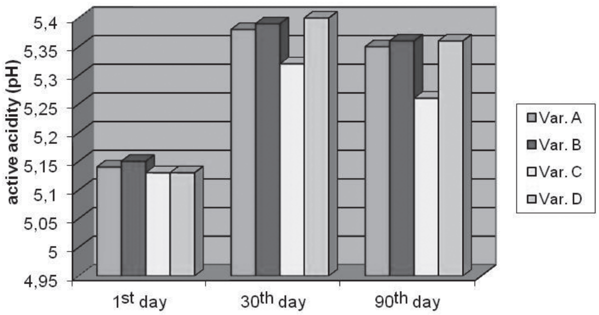

Figure 1. Dynamics of pH during the ripening period

Table 3. Chemical composition of the examined Kashkaval samples (n=5)

Dry matter (%)		F= **97.09	
	1st day	30th day	90th day
A (control)	54.12±1.79	60.86±0.98	63.78±0.39
B (emulsion)	54.18±0.82	60.02±0.99	62.90±0.86
C (wax)	54.69±1.41	59.05±0.29	60.60±0.55
D (foil)	54.49±0.44	59.21±0.49	60.10±0.22
Fat (%)		F= ns3.07	
A (control)	27.96±0.15	28.11±0.48	28.87±0.75
B (emulsion)	27.93±0.29	28.50±0.55	29.16±0.72
C (wax)	28.01±0.63	28.65±0.50	29.35±0.39
D (foil)	28.00±0.19	28.68±0.18	29.55±0.20
Proteins (%)		F= **27.02	
A (control)	11.45±0.55	17.87±0.65	23.52±0.81
B (emulsion)	11.45±0.19	17.88±0.86	22.80±0.98
C (wax)	11.48±0.34	17.68±0.65	21.87±0.62
D (foil)	11.39±0.43	17.50±0.28	20.58±0.52
Ash (%)		F=**8.16	
A (control)	2.43±0.26	3.87±0.21	4.66±0.23
B (emulsion)	2.31±0.18	3.74±0.29	4.63±0.22
C (wax)	2.33±0.15	3.38±0.26	4.32±0.29
D (foil)	2.37±0.12	3.45±0.20	4.21±0.22

ns - is not statistically significant; *level of significance p<0.05;
**level of significance p<0.01 ($F_{0.05}$=3.13 for p<0.05; $F_{0.01}$=5.01 for p<0.01)

Chemical characteristics of Kaskaval during ripening are presented in Table 3. The highest barrier characteristics were detected for the sample coated by a polymer foil with dry matter after 90 days was 60.10 % while the control sample showed the highest moisture loss and had 63.78 % of the total dry matter. Our results for dry matter in Kashkaval corresponded with results presented by Andronoiu et al. (2015), Mijačević and Bulajić (2004) and Kindstedt et al. (2004).

Protection with polymer foil contributes to keeping the moisture inside the Kashkaval, resulting in higher yields and better profitability for the dairy factories. On the other hand, higher moisture content can cause bitter taste in the later maturing period, because of more intensive proteolysis. The milk fat content in the Kashkaval cheese affects the flavour and consistency of the product. For a fact, cheeses with higher fat contents have softer consistency, while cheeses with lower fat contents are usually firmer.

Table 4. Nitrogen fractions of Kashkaval during ripening (n=5)

Total nitrogen		F= **31.93	
	1st day	30th day	90th day
A (control)	1.7962±0.0852	2.8015±0.1023	3.6877±0.1272
B (emulsion)	1.7948±0.0299	2.8037±0.1340	3.5746±0.1533
C (wax)	1.8009±0.0543	2.7721±0.1022	3.4282±0.0972
D (foil)	1.7867±0.0688	2.7433±0.0434	3.2269±0.0818
Soluble nitrogen		F= **27.20	
A (control)	0.3110±0.0128	0.4910±0.0292	0.6995±0.0416
B (emulsion)	0.3122±0.0148	0.5323±0.0097	0.7445±0.0266
C (wax)	0.3155±0.0181	0.5493±0.0083	0.8094±0.0530
D (foil)	0.3097±0.0136	0.5212±0.0102	0.8641±0.0481
Insoluble nitrogen		F= **41.86	
A (control)	1.4852±0.0802	2.3105±0.1315	2.9882±0.1183
B (emulsion)	1.4826±0.0151	2.2714±0.1159	2.8301±0.1799
C (wax)	1.4853±0.0583	2.2228±0.0806	2.6188±0.0874
D (foil)	1.4770±0.0824	2.2221±0.0336	2.3628±0.1171
Primary nitrogen products		F= **138.15	
A (control)	0.2460±0.0100	0.4214±0.0189	0.5245±0.0210
B (emulsion)	0.2495±0.0056	0.4612±0.0102	0.5654±0.0139
C (wax)	0.2485±0.0075	0.4772±0.0091	0.6113±0.0049
D (foil)	0.2466±0.0106	0.4525±0.0114	0.6640±0.0062
Secondary nitrogen products		F= **43.31	
A (control)	0.0650±0.0028	0.0696±0.0021	0.1750±0.0040
B (emulsion)	0.0627±0.0029	0.0711±0.0037	0.1791±0.0091
C (wax)	0.0670±0.0019	0.0721±0.0020	0.1981±0.0062
D (foil)	0.0631±0.0028	0.0687±0.0019	0.2001±0.0036
Coefficient of maturity		F= **41.87	
A (control)	17.33±1.04	17.55±1.72	18.98±1.32
B (emulsion)	17.39±0.65	19.01±1.25	20.85±1.69
C (wax)	17.53±1.22	19.83±0.97	23.62±1.58
D (foil)	17.35±0.87	19.00±0.43	26.79±1.89

ns - is not statistically significant; *level of significance $p<0.05$;
**level of significance $p<0.01$ ($F_{0.05}=3.13$ for $p<0.05$; $F_{0.01}=5.01$ for $p<0.01$)

After three months from the production date, samples which contained the highest fat content were protected with wax and polymer foil, which are materials known do not allow the fats to migrate at the cheese surface. Similar results regarding fat of Kashkaval cheese were reported by Marinova et al., (2016), Mijačević et al., (2005) and Ayar (1991).

Ash content affects the rheological properties of Kashkaval cheese, participates in metabolic processes of microorganisms, and catalyzes enzymatic processes. Loss of moisture in the cheese during the ripening has inversely proportional influence on the ash content. Our results are in accordance with the research of Ayar (1991), Santa and Srbinovska (2014) and Marinova et al. (2016).

Proteolytic changes of Kashkaval are shown in Table 4. In *pasta filata* cheeses, one of which is also Kashkaval, activity of the rennet on α_s casein is limited due to high temperatures during the stretching of the curd (*baskija*).

The total amount of nitrogen increased continuously during ripening in all four examined samples. Different packaging of Kashkaval had a significant influence on the total amount of nitrogen (F=31.93) where the highest amount (3.6877 %) was found in the control sample and the lowest content (3.2269 %) was found in the sample protected with foil. Those differences were probably related to a decrease in moisture during ripening and a different concentration of other parameters. Similar results for dynamics of total nitrogen were reported by Mihajlov (2003) on Cheddar cheese, Kocak et al. (2005) for Turkish kashkaval-type cheese Kashar and Jovanović et al. (2007) for semi-hard cheese based on milk protein coaggregates.

The soluble nitrogen is one of the indicators indicating the degree of proteolysis intensity in Kashkaval cheese. According to Kožev (2006), protein hydrolysis in Kashkaval starts with cheddarization of *baskija* where approximately 2.5 to 4 % is transformed into the water soluble nitrogen. The highest amounts of soluble nitrogen were found in samples protected with higher barrier characteristics material - polymer foil (0.8641) and wax (0.8094). These materials obviously enabled better conditions for development of the present microflora and its' enzymes. The obtained results showed a good correspondence with findings reported by Tratnik and Božanić (2012) which note that besides other factors, higher levels of proteolysis was connected with higher moisture and water activity in cheese. Similar results were obtained by Zaharia (2012), Tarakci and Kucukoner (2006) and Gürsoy (2009). Non-soluble nitrogen had the opposite tendency, control sample and sample protected with polymer emulsion had lower degree of proteolysis and therefore a higher content of non-soluble nitrogen. Different protection of the *Kashkaval* rind had a significant influence ($p<0.01$) on both, soluble and non-soluble nitrogen fraction.

According to Benfeldt et al. (1997) the primary nitrogen products (PNP) are a result of primary proteolysis of the cheeses which mainly depends on the residual rennet and the present plasmin in the cheeses. In all of the examined samples of *Kashkaval* PNP continuously increased during ripening, which on the 90th day reached the maximum in sample D with 0.6640, while the minimum value was determined for sample A with 0.5245. The observed differences were most probably due to a lower moisture content and a slower proteolysis in sample A. Variants protected with materials with higher barrier characteristics do not have such a big loss of moisture and we can notice faster degradation of proteins.

Secondary nitrogen products (SNP) are formed during secondary proteolysis in Kashkaval under influence of proteinases and peptidases of lactic acid bacteria. Content of SNP at the beginning of the ripening process was low because of the negative effect on microorganisms as a result of high temperatures stretching the baskija. After 3 month ripening period, the lowest value of SNP was detected in control variant with 0.1750% and the highest result had variant protected with polymer foil with 0.2001 %.

Similar results regarding the dynamics of SNP on semi-hard cheese were reported by Jovanović et al., (2007), while Mihajlov (2003) showed higher concentrations (0.32431-0.43431 %) for Cheddar cheese. Such differences in results for Cheddar cheese are most probably a result of different applied starter cultures, technological processes, fast vacuum packaging, and different ripening conditions. Analyses of variance showed significant statistical influence of packaging materials on the concentration of primary and secondary nitrogen products.

Ripening dynamics of cheeses is usually monitored by a coefficient of maturity which presents the relation between soluble and total nitrogen. The examined samples of Kashkaval showed a continuous increase of the coefficient which was higher at variants protected with materials which have higher barrier characteristics. The lowest coefficient of maturity was found for the control sample (18.98 %) at 90th day of the production, while the highest values were determined for samples protected with polymer foil (26.79 %). Similar results were reported by Jovanović et al. (2007) for semi-hard cheese and Popović-Vranješ et al. (2009) for Trapist type cheese.

The calculated theoretical yields of examined cheese samples after 90 aging days were as following - sample A (8.689 %), sample B (8.814 %), sample C (9.156 %) and sample D (9.234 %). The highest abatement was determined at the control sample. Sample B, which was protected with polymer emulsion, had a slightly better yield taking into account that *Plasticoat* does not prevent the abatement, but ensures a right ripening direction of the Kashkaval and protects the cheese from negative influences like appearance of moulds, yeasts and rind bacteria.

Conclusion

Based on our results, the examined packaging materials significantly influenced the chemical composition, the degree of proteolysis and the yield of the Kashkaval cheese. The polymer emulsion was found as the best option for rind protection in the ripening process, since it enabled the production of Kashkaval with standard characteristics unlike the samples protected with wax and polymer foil.

Utjecaj materijala za pakiranje na kvalitetu Kačkavalja

Sažetak

U ovom radu ispitivan je utjecaj različitog ambalažnog materijala (A - kontrolni uzorak, B - polimerna emulzija, C - vosak i D - polimerna folija) na kvalitetu Kačkavalja. Najnižu pH vrijednost imao je uzorak zaštićen voskom, što je rezultat zadržavanja nastalih organskih kiselina i plinova od strane ambalažnog materijala. Statistički značajan utjecaj ambalažnih materijala ($p<0.01$) bio je utvrđen kod sadržaja suhe tvari, proteina i pepela, dok statistička značajnost nije bila utvrđena kod sadržaja masti kod Kačkavalja. Proteolitički procesi bili su izraženiji kod uzorka zaštićenog voskom i polimernom folijom, s višim razinama topljivog dušika, primarnih i sekundarnih dušičnih spojeva i koeficijenta zrelosti u odnosu na kontrolni uzorak i uzorak zaštićen polimernom emulzijom.

Ključne riječi: Kačkavalj, zaštita kore, zrenje, ambalažni materijali

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