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Food Applications of Monolayer LDPE/Bioactive Nanocomposite Films

M. Ionescu[*], G. Mustatea[*], V. Ionescu[*], G. Spadaro[*], Z. Vuluga[**], M. Iorga[**] and D. Florea[**]

[*] Institute of Food Bioresources, Bucharest, Romania

[**] National Research & Development Institute for Chemistry and Petrochemistry ICECHIM, Bucharest, Romania

Abstract: Recently, related to functional food development, is building a new packaging technology called bioactive packaging, in which a package or cover for a package have the unique role in growing food impact on consumer health. For bioactive packaging concept development we have to point the industrial benefits of bioactive compounds which will be included in packaging or coating materials, beyond their direct inclusion in food. In this study were analyzed various types of monolayer LDPE / bioactive nanocomposite films, obtained by incorporating organophylized silicate modified with starch, hydrolyzed collagen, fatty acid C_{16-18} and quebracho (a natural poly-phenol). For food packaging applications were taken into account both the requirements of food contact legislation and physico-mechanical characteristics, water vapors and gas permeability. Packaging experiments of 2 types of products were carried out on meat products: smoky pork salami and chicken meat paste (sausage) and high quality cow cheese. The two types of products were investigated by physico-chemical analysis and microbiological analysis periodically during storage, at different times, depending on the package product shelf-life.

Keywords: nanocomposite, bioactive, food application, packaging

1. Introduction

Technical properties of various packaging materials and their actual use will depend, mostly, on price and availability in their particular field.

Nanocomposite-based polymeric materials have gained in popularity for a wide range of applications, with improvement of all products and commercialization of products that exploit their unique mechanical and thermal properties [1].

Development of monolayer nanocomposite polymers films used as food packaging involves the incorporation and/or controlled release of bioactive compounds, with direct impact on consumer health [2].

Production technologies include new integration technologies, micro- and nanoencapsulations, encapsulations of enzymes and/or immobilized enzymes. It was found that all these technologies have excellent allies in private properties of biopolymers [3].

Legislation requirements: if efforts in traditional food packaging field were moving towards minimizing the interaction between food and packaging material, mater settled long time ago and provided by a clear legislation, recently, has become a new trend in new packaging materials development.

Therefore, regulation (EC) No. 1935/2004 authorizes placing on the market two types of packages, which acts "active" and "intelligent" in contact with food by providing information about the quality (freshness) of the product or by its preservation for more time, by introducing favorable chemical changes.

2. Experimental

Tested monolayer films:

- Low-density polyethylene with polyethylene-*g*-maleic anhydride copolymer (M1 LDPE);
- Low-density polyethylene with polyethylene-*g*-maleic anhydride copolymer and organophilized silicate (Cloisite 20A) modified with hydrolyzed collagen (C08G), quebracho (QBR), cornstarch (Amp) and fatty acid C_{16-18}.

The films, with 35-70 μm thickness, were obtained by blow-extrusion at 160± 5°C. The obtained films were marked as: D20A, D20A-QBR, D20A-C_{16-18} and D20A-Amp.

Test methods used in laboratory cover with:

- Test method for overall migration analysis of food contact materials from packages;
- Organoleptic examination;
- Physico-mechanical characteristics analysis;

Testing in practical conditions included: samples packaged (filling) in a meat products factory, and also samples packaged of high quality cow cheese.

The quality of packaged products was carried out by physico-chemical and microbiological analyses, periodically, during storage, at temperatures recommended by producer.

Overall migration

Overall migration of components, express in mg/kg (ppm) or mg/dm^2, consists in determination of the totality of substances that migrate into the extraction media, from food contact materials.

Test conditions for tested material have followed the following regulatory provisions: SR EN 1186-1/2003 and SR EN 1186-9/2003.

TABLE 1. Packaged samples

Chicken meat paste (sausage)	Smoky pork salami	Cheese
D20A-C08G	D20A-C08G	D20A-C08G
D20A-QBR	-	D20A-QBR
D20A-C_{16-18}	-	D20A-C_{16-18}
D20A-Amp	D20A-Amp	D20A-Amp
-	M1 – LDPE	M1-LDPE

Organoleptic examination

Organoleptic test has been carried out with the help of sensory analyzers (sense organs and senses) used as tools for analysis and measurement.

Organoleptic examination run by the method of comparison compares samples of material under extraction and extracts with control samples and liquids extraction (food or food simulants which have not been in contact with the material under examination).

Under current legislation, GD no. 1197/2002 for approving the Norms regarding materials and objects coming into contact with foodstuffs, packages must, under normal conditions of use, not to transfer constituents to foodstuffs in quantities which could endanger human health or could bring an unacceptable change in the composition of food or deterioration in the organoleptic characteristics.

Samples of packages and packaging materials, foods or food simulants must not submit organoleptic changes (color, smell, taste, where possible), compared with control samples.

Gas permeability and water vapors permeability tests

Barrier properties were determined by specific analyses:

- Determination of water vapors transmission rate according to SR EN ISO 15106-1:2005 (humidity detector method);
- Determination of gases transmission rate through plastic films according to DIN 53380-1 (manometric method);

3. Results and Discussions

Packaging materials analysis

Overall migration tests

It was studied the overall migration in simulant A (distilled water), simulant B (3% acetic acid solution), simulant C (10% ethylic alcohol solution), in food contact conditions: extraction ratio 1:1 (fill), 10 days at 40 ^{0}C and in stimulant D (ethylic alcohol 95%), 24 hours at 40 ^{0}C, in the same extraction ratio. After immersion in simulant both sample and extraction liquid were sensory analyzed. The results are presented in Table 2.

TABLE 2. Overall migration test results

Sample	Overall migration (mg/dm^2)			
	Aqueous simulans			Fatty simulants
	A (Distilled water)	B (3% Acetic acid)	C (10% Ethylic alcohol)	D (95% Ethylic alcohol)
M1 LDPE	8,16	8,0	2,5	2,33
D20A-C08G	10,16	8,83	4,16	6,0
D20A-QBR	9,50	8,66	3,83	6,16
D20A-C_{16-18}	9,16	9,0	2,50	17,16
D20A-Amp	10,83	10,33	4,66	2,33

The values of overall migration in aqueous simulants (A, B and C) are below the limits of 10 mg/dm^2 (+1 mg/dm^2) imposed by GD no. 1197/2002. Small exceeds were founded at D20A-Amp sample.

The values of overall migration in D simulant (ethylic alcohol 95%) are below 10 mg/dm^2 (+1 mg/dm^2) limit. The only exceeded value is at D20A-C_{16-18} sample.

Gases and water vapors permeability analysis

Results of the analysis of gas permeability in the series with organophilized modified silicate are presented in Table 3. Compared to blank (M1PE-MA), it ranks lower in all the tested films; the same for water vapors permeability at 23 °C. Exceptions for water vapors permeability at 38 °C: D20A-C_{16-18} sample is higher than blank.

TABLE 3. Permeability analysis results

Sample	PERMEABILITY (P)				
	water vapors (g/m^2·24h)		gases (cm^3/m^2·24h·bar)		
	at 23 ºC	at 38 ºC	O_2	N_2	CO_2
M1 LDPE	5,02	9,46	4484	973,83	10916
D20A-C08G	4,16	7,29	1720	506,39	5870
D20A-QBR	2,24	9,23	1859	887,46	10160
D20A-C_{16-18}	2,77	11,01	2364	869,31	9931
D20A-Amp	1,72	5,74	1352	466,02	5261

Packaged food analysis

Physico-chemical parameters analysis: protein, collagen, fat, sodium chloride, humidity and water activity;

The final product was analyzed after 21 days to estimate the influence of package over physico-chemical properties after certain storage period. The results are presented in Table 4 and Table 5 and in Figure 1.

Between the four tested films there are no significant modifications; only collagen content had a small difference in **D20A-C_{16-18}** (highest value) and **D20A-Amp** (lowest value) samples.

Regarding other parameters, practically, we can consider they did not vary with film type.

TABLE 4. Physico-chemical parameters for chicken meat paste

Sample	CHICKEN MEAT PASTE (SAUSAGES)					
	PHYSICO-CHEMICAL PARAMETERS					
	Protein (%)	Collagen (%)	Fat (%)	NaCl (%)	Humidity (%)	Water activity
D20A-C08G	11,45	3,38	21,00	2,79	63,80	0,942
D20A-QBR	11,13	3,11	20,52	2,69	63,59	0,970
D20A-C_{16-18}	11,53	3,92	21,45	2,46	63,21	0,976
D20A-Amp	11,78	2,64	20,73	2,15	63,69	0,978

TABLE 5. Physico-chemical parameters for salami

Sample	SMOKY PORK SALAMI					
	PHYSICO-CHEMICAL PARAMETERS					
	Protein (%)	Collagen (%)	Fat (%)	NaCl (%)	Humidity (%)	Water activity
M1 LDPE	12,21	2,61	20,06	1,81	63,47	0,986
D20A-C08G	12,13	2,43	22,35	2,13	61,63	0,982
D20A-Amp	12,19	2,10	20,14	1,69	63,13	0,985

Between the three tested films there are no significant modifications; at D20A-C08G film fat and NaCl content are slightly higher and the humidity is slightly lower.

Regarding water activity we can observe higher values (after 21 days) in salami samples. However between all tested samples no significant differences were observed.

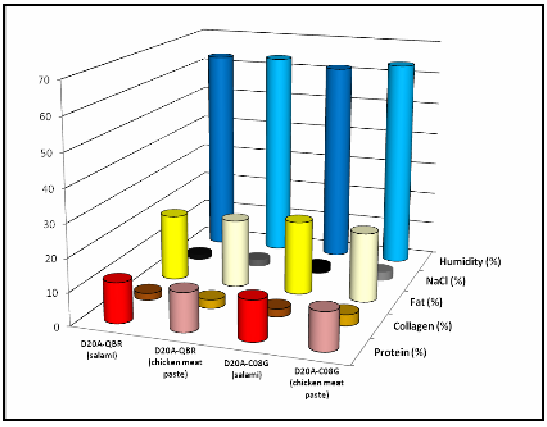

Figure 1. Physico-chemical parameters

Easily hydrolysable nitrogen

As we can observe from analyzing values in Table 6, easily hydrolysable nitrogen – chicken meat paste, shows a slight variation during the 21 days storage time; so it can see a higher growth on **D20A-Amp** and **D20A-C_{16-18}**, but the values are below limit imposed.

Easily hydrolysable nitrogen – salami record a continuous growth during the 3 weeks storage time, also it can see a higher growth on **D20A-Amp.**

For results evaluation it can be considered the limit values from Order no. 975/1998 for the content of easily hydrolysable nitrogen (resulted from proteolysis process performed by microorganisms) respectively maximum permissible for salted or smoked meat of 45 g NH_3/100mg.

TABLE 6. Easily hydrolysable nitrogen – chicken meat paste

Storage time / Sample	Initially	7 days	14 days	21 days
	Easily hydrolysable nitrogen (mg/100g)			
D20A-C08G	27,5	32,3	28,9	30,56
D20A-QBR	27,5	35,7	27,25	30,56
D20A-Amp	27,5	34,0	33,73	35,42
D20A-C_{16-18}	27,5	22,1	28,98	34,0

TABLE 7. Easily hydrolysable nitrogen – salami

Storage time Sample	Initially	7 days	14 days	21 days
	Easily hydrolysable nitrogen (mg/100g)			
D20A-Amp	27,5	37,0	38,04	47,13
M1 LDPE	27,5	32,1	35,77	42,27
D20A-C08G	27,5	32,0	37,43	42,11

Cheese analysis

Acidity values for tested cheese samples show a different variation, during 10 weeks storage, depending on film type thus: growth for **D20A-QBR** and **D20A-C_{16-18}** films and decrease for other (**M1 LDPE**, **D20A-C08G** and **D20A-Amp**).

One explanation may be based on better barrier properties (in first case), when as result of microbial metabolism CO_2 is produced, which is dissolved in water from product conducting on acidity growth. In *Figure 2* is shown the acidity evolution during storage period.

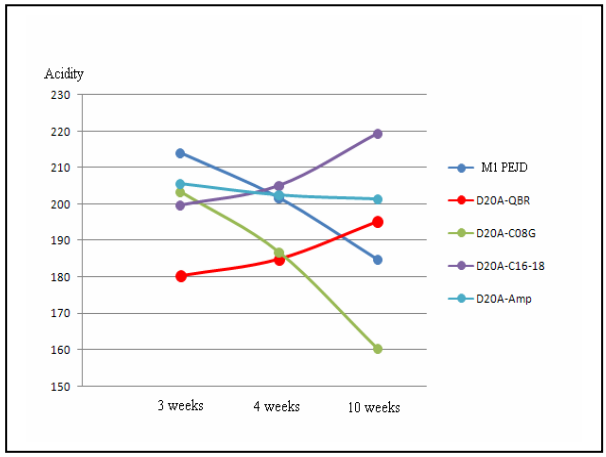

Figure 2. Evolution of tested sample acidity during storage period

The humidity of the samples was 52.27 % initially. As can be seen from *Table 8*, the humidity decreased for all tested samples, the lowest value being recorded for **D20A-C_{16-18}** sample, result correlated with water vapors permeability result, slightly higher than other samples.

Regarding **D20A-QBR** and **D20A-Amp** the humidity levels are maintained at close values and higher than the other; a phenomenon also correlated with water vapors permeability results of these samples.

TABLE 8. Water activity, humidity and organoleptic examination of tested samples

Sample	Water activity *	Humidity (%) *	Organoleptic exam *
D20A-QBR	0,933	49,52	Small spots of mold on the side
D20A-C08G	0,957	44,80	Small spots of mold on surface
D20A-C_{16-18}	0,962	41,30	No modifications on surface
D20A-Amp	0,958	48,61	No modifications on surface
* Tests were made after 10 weeks of storage			

Microbiological analysis

Analysis of total number of germs (TNG) – chicken meat paste (see Table 9), shows good values even after 3 weeks of storage, for 3 of tested samples (**D20A-QBR**, **D20A-Amp** and **D20A-C08G**), 10^2/g order, compared to **D20A-C_{16-18}** sample, 10^5/g order, which represent maximum allowed amount (DS/EN ISO 4833:2003).

TABLE 9. Total germ – chicken meat paste

Storage time / Sample	Initially	7 days	14 days	21 days
	TNG (cfu/g)			
D20A-C08G	< 10	$2.8 \cdot 10^2$	$3.3 \cdot 10^2$	$5.2 \cdot 10^2$
D20A-QBR	< 10	< 10	< 10	$1.5 \cdot 10^2$
D20A-Amp	< 10	< 10	$2.1 \cdot 10^2$	$4.0 \cdot 10^2$
D20A-C_{16-18}	< 10	$4.5 \cdot 10^2$	$3.2 \cdot 10^5$	$4.9 \cdot 10^5$

Analysis of total number of germs (TNG) – salami (see Table 10), shows good values up to 2 weeks of storage, below limit of 10^5/g for **D20A-Amp** sample.

Other tested samples (**D20A-C08G** and **M1-LDPE**) don't meet the microbiological requirements, even after 2 weeks storage time.

TABLE 10. Total germ – salami

Storage time / Sample	Initially	7 days	14 days	21 days
	TNG (cfu/g)			
D20A-Amp	< 10	6.3 · 10	$7.7 \cdot 10^4$	$4.9 \cdot 10^6$
M1 LDPE	< 10	6.3 · 10	$9.2 \cdot 10^6$	$6.2 \cdot 10^7$
D20A-C08G	< 10	6.3 · 10	$9.0 \cdot 10^7$	$1.0 \cdot 10^8$

Analyzing Figure 3 we can see a different variation of yeasts and molds as follows:

- Regarding **D20A-Amp** sample we can observe an increase of this parameter value until de 20th day, after which remains practically constant until 28th day.
- Regarding other samples (**D20A-C08G**, **D20A-QBR**, and **M1 LDPE**) we can observe similar variation, so in the 28th day the values are slightly closed, but higher than those of D20A-Amp sample.
-Regarding D20A-C_{16-18} sample we can observe the strongest development of yeast and molds.

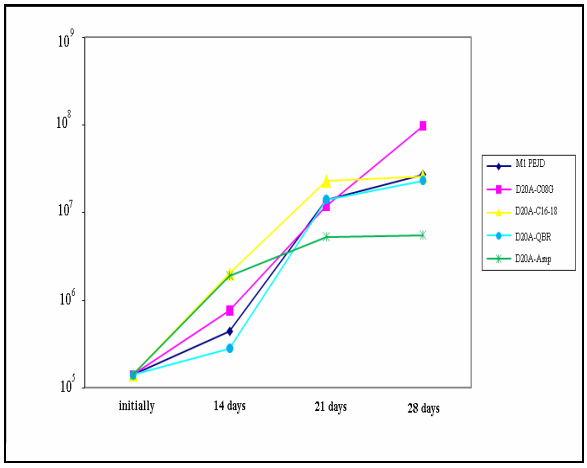

Figure 3. Variation of yeasts and molds

Because the values of this microbiological parameter are high the experiments should be repeated under controlled packaging conditions, considering that the cheese packaging was made in normal atmosphere, in laboratory conditions.

4. Conclusions

Easily hydrolysable nitrogen content (expressed as NH_3) and water activity values, after 21 days, of salami samples are above the values of chicken meat paste samples, which can be explained by the difference between the two products composition.

The results of physico-chemical analysis and the results of gases and water vapors permeability tests are according to microbiological analyses results.

Thus, analysis of NTG – chicken meat shows very good values even after 3 weeks storage time, for all tested samples, exception D20A-C_{16-18} (sample with highest water vapors permeability at 38 ^{0}C), while analysis of NTG – salami shows very good values up to 2 weeks of storage only for D20A-Amp.

In D20A-Amp and D20A-QBR samples the humidity values of cheese, during 10 weeks of storage, maintain at similar values and higher than others, phenomenon also correlated with water vapors permeability results. Increased acidity of cheese sample packed in D20A-Amp film during 10 weeks of storage time can be explained by better barrier properties at water vapors and gases, when, as a result of microbial metabolism is produced CO_2 which dissolves in water from product leading to an increased acidity.

These results recommend the use of D20A-Amp, D20A-C08G and D20A-QBR for chicken meat paste packaging, but only after checking physico-chemical properties which influence their conduct during filling and subsequent thermal treatments.

In addition, better barrier properties at water vapors and gases and microbiological analysis results recommend the use of variants of D20A-Amp to cheese packaging.

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