CHARACTERIZATION OF NANOCOMPOSITE POLYMER FILMS USED FOR FOOD PACKAGING

M. Ionescu[1], G. Mustatea[1], G. Spadaro[1], Z. Vuluga[2], D. Florea[2]
[1]Institut of Food Bioresources , Dinu Vintila Street no.6, Bucharest
[2]INCDCP - ICECHIM, Splaiul Independentei no.202, Bucharest
E-mail: ionescu_mrn07@yahoo.com

Abstract
Development of monolayer films based on polymeric nanocomposites used in food packaging presumes incorporation and/or controlled release of some bioactive components from composite biomaterials, having direct impact on the consumer's health.
Variants for obtaining bioactive nanocomposites by incorporating an organophilised silicate modified with starch, hydrolyzed collagen, fatty acid C_{16-18} and quebracho (a natural poliphenol) were selected during the study.
Monolayer films obtained of LDPE/silicate modified with bioactive properties nanocomposites, nanostructured, were characterized in terms of morphostructural properties (XRD analysis, TGA analysis and DSC analysis), mechanical (tensile strength, elongation at break). Preliminary tests of interaction of these materials with food, in laboratory conditions, were conducted.
Testing methodology used by the laboratory included: overall migration analysis of components from food packaging, specific migration analysis of bioactive components (by UV-VIS spectrophotometry), organoleptic examination, gases permeability analysis (O_2, N_2, CO_2), water vapor permeability analysis and heavy metal analysis (specific migration and content) by AAS.

Keywords: nanocomposites, bioactive components, silicates

1. INTRODUCTION

Food packaging has developed strongly during recent years, mainly due to increased demands on product safety, shelf-life extension, cost-efficiency, environmental issues, and consumer convenience. In order to improve the performance of packaging in meeting these varied demands, innovative modified- and controlled - atmosphere packaging, and active and intelligent packaging system are being developed, tested and optimized in laboratories around the world [1].
Polyethylene (PE) is preferred for film fabrication used as packages in both food and medical industries [2].
In order to obtain the properties asked by the application (high stiffness, dimensional and thermal stability, toughness, processability and barrier properties) polymer nanocomposites with molecular dispersed layered silicate are preferred [3].

2. MATERIALS AND METHODS

- Low-density polyethylene (LDPE);
- Organophilized silicate;
- Functionalized polymer: polyethylene-graft- maleic anhydride (PE-MA);
- Bioactive substances: hydrolyzed collagen from bone gelatin (HO_8G), quebracho (QBR), corn starch (Amp), fatty acid C_{16-18}.

Test methods used in laboratory cover with:

- Test method for overall migration analysis of food contact materials from packages;
- Test method for specific migration of bioactive components;
- Organoleptic test;
- Gas permeability and water vapors permeability test;
- Content analysis of heavy metals;
- Morphostructural properties test;
- Mechanical properties test.

Overall migration of components test
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.

Organoleptic test

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, examining samples of material under extraction and extracts compared with control samples and liquids extraction (food or food simulants which have not been in contact with the material under examination).
Under legislation in force that H.G. no. 1197/2002 for approving the Norms regarding materials and objects coming into contact with foodstuffs, must, under normal conditions of use does not transfer constituents to foodstuffs in quantities which could endanger human health or could bring an unacceptable change in the composition of food or a deterioration in the organoleptic characteristics thereof.
Samples of packaging and packaging materials, foods or food simulants must not submit organoleptic changes (color, smell, taste, where possible), compared with control samples.

Bioactive components specific migration analysis by UV/VIS spectrometry
Release of bioactive compounds in simulant A (distilled water) in conditions of contact with food (40 □C, extraction ratio 1:1), gradually, over 10 days contact has been studied. Aqueous extract was analyzed by UV/VIS spectrophotometer type JASCO 550, at the characteristic wavelength and concentration in simulant A gave each bioactive compound was calculated.
UV spectra recorded at the wavelength corresponding to maximum absorption (for quebracho was taken into account the absorbance values at 279 nm) were analyzed.

Gas and water vapor permeability analysis

Barrier properties to water vapor and gases expressed by the permeability were determined by
specific analysis:

- Determining transmission rates of water vapor according to DIN EN ISO 15106-1: 2005 (method of moisture detection);
- Determining gas transmission rate through plastic films and foils according to DIN 53380-1 (manometric method).

Heavy metals content analysis

Analysis of lead and cadmium content from plastic materials acetic extracts

Acetic extract: 3% acetic acid solution that have been in contact with test samples in extraction ratio 1:1, temperature: at 400C, in accordance with DIN EN 1186-9 / 2003.
Lead (Pb) and cadmium (Cd) release analysis was performed by AAS – Graphite Furnace Technique with "AAnalyst 600" atomic absorption spectrophotometer.
Analysis of lead, cadmium, total chromium and mercury in final products
Analysis followed two steps:

- Mineralization method in microwave oven;
- Analysis of metal concentration by AAS, as follows:
  - Lead, cadmium, chromium (total) - with atomic absorption spectrophotometer "AAnalyst 600" - the graphite furnace technique;
  - Mercury - with atomic absorption spectrophotometer "AAnalyst 400" which was adapted system Perkin-Elmer MHS 15, cold mercury vapor generation technique;

Morphostructural properties analysis
The morphostructural properties were analyzed by X-ray diffraction (XRD), thermo gravimetric analysis (TGA) and differential scanning calorimetry analysis (DSC).
The basal spacing, d_{001}, was determined by means of X-ray diffraction (XRD) on a DRON-2, 0 X-ray diffractometer with horizontal goniometer; it was utilized the CoKα radiation source (λ = 1.79021 Å) filtered with Ni for Kβ

component removing, in Bragg-Brentano system (by reflection); the patterns were automatically recorded at small angles (2θ = 2÷30°).
Nanocomposites thermal analyses was done on a Netzsch DSC-TGA type STA 449 C-Jupiter, with the heating rate of 10°C/min, under a current of He of 25cm^3/min and in the temperature interval of 30-750°C.

Mechanical properties analysis
The mechanical properties, Tensile strength (σb), Elongation at break (εb), were determined according to SR ISO 37:1997.

3. RESULTS AND DISCUSSION

Overall migration test results
Analyzing Table 1 we can see:
- The overall migration results in aqueous simulants (distilled water and 3% acetic acid solution) are under the 10 mg/dm^2 limit (+1 mg/dm^2 analytical tolerance). Very modest excess is found in the 2 different starch samples (D20A-Amp and DAmp).

Table 1 Overall migration test results

Sample name	Overall migration (mg/dm^2)			
	A Distilled water	B Acetic acid 3%	D Iso-octane	D Ethylic alcohol 95%
M PEJD	9,16	7,50	9,0	0,83
M1 PEJD - PE-MA	8,16	8,0	23,66	2,33
D20A	6,16	5,0	16,16	6,0
D20A – C08G	10,16	8,83	26,0	6,0
D20A – QBR	9,50	8,66	16,83	6,16
D20A – C_{16-18}	9,16	9,0	40,33	17,16
D20A – Amp	10,83	10,33	27,33	2,33
DAmp	11,33	12,0	23,50	7,16
Test conditions	10 days at 40 □C		24h at 40 □C	

The overall migration results in fatty simulant (95% ethylic alcohol solution) are under the 10 mg/dm^2 limit (+1 mg/dm^2 analytical tolerance). The only value exceeded is found in fatty acid sample (D20A-C_{16-18}).

- The overall migration results in fatty simulant (isooctane) are all over the 10 mg/dm^2 limit (+3 mg/dm^2 analytical tolerance).

Organoleptic test

Organoleptic examination results have shown no changes to any of the materials tested.

Specific migration test results

Table 2 Specific migration test results

D20A-QBR film		
Test conditions	Absorbance (279 nm)	Quebracho release (mg/dm^2)
1 day / 40 ^{0}C	0,04410	0,32
2 days / 40 ^{0}C	0,06540	0,47
3 days / 40 ^{0}C	0,06929	0,50
7 days / 40 ^{0}C	0,07460	0,54
8 days / 40 ^{0}C	0,06703	0,48

Regarding the release of bioactive compounds in A simulant (distilled water), in 1:1 extraction ratio, at 40^{0}C, was studied only D20A-QBR sample, in pursuing the release of quebracho periodically during 10 days contact.

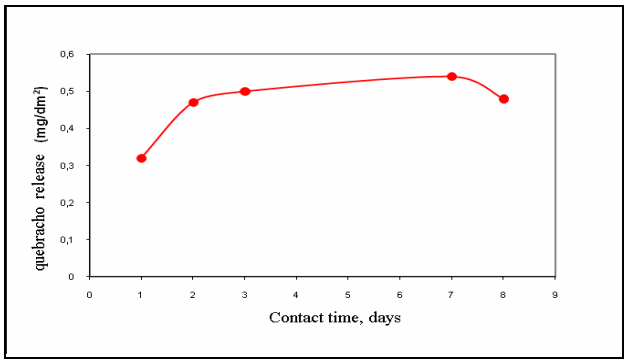


Figure 1 Quebracho release

It is noted that the maximum absorption is at 279 nm. Also we can observe the increase of absorbance, gradually, during the first 7 days after which the absorbance decreases.

In the first 2 days the amount of QBR released in A stimulant significantly increase, after which growth is very slow until the 7th day, then begins to decrease. Thus, the maximum amount of released QBR: 0.54 mg/dm^2 may explain the increase of global migration value in A simulant over M1 control sample.

Permeability test results

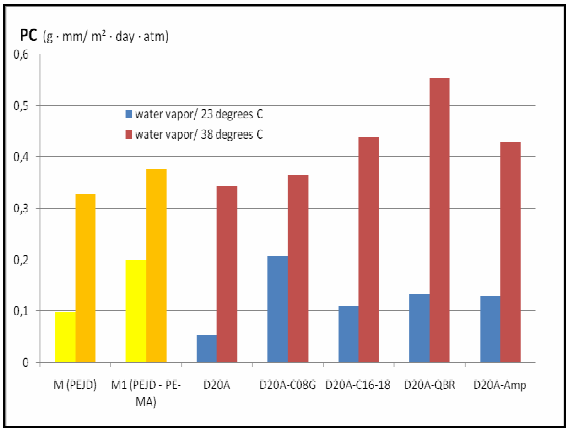


Figure 2 Water vapor permeability coefficients

Analyzing the results of gas permeability, it ranks lower in comparison with blank for all types of films.

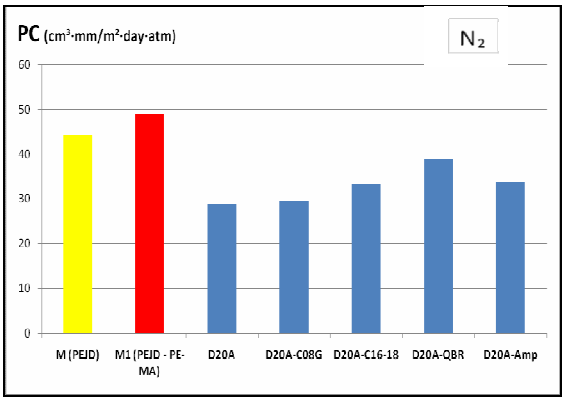


Figure 3 Oxygen permeability coefficients

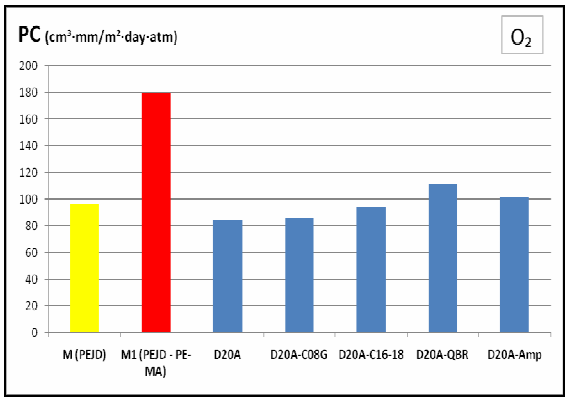


Figure 4 Nitrogen permeability coefficients

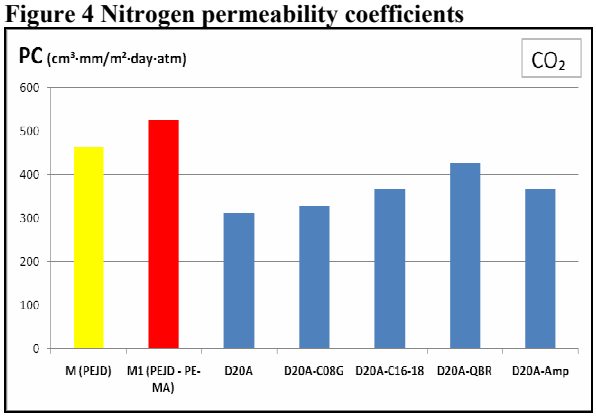


Figure 5 Carbon dioxide permeability coefficients

Heavy metals content analysis results

Table 3 Heavy metal migration

Sample	Heavy metal migration (ppb)	
	Pb	Cd
M PEJD	0,661	0,058
M1 PEJD - PE-MA	3,443	0,069
D20A – C08G	1,366	0,047
D20A – QBR	0,799	0,040
D20A – C_{16-18}	3,046	0,128
D20A – Amp	1,478	0,042
DAmp	1,218	0,033

Analyzing the results can be seen a low content of heavy metals (Pb, Cd) in both acid extract and final product (film), for each of the 4 metals analyzed, which is compliance with regulations specified.

Table 4 Heavy metal content

Sample	Heavy metal content (ppm)			
	Pb	Cd	Cr (total)	Hg *
M PEJD	0,518	0,012	0,035	<LD
M1 PEJD - PE-MA	0,322	0,010	0,851	<LD
D20A – C08G	0,476	0,017	0,180	<LD
D20A – QBR	1,060	0,019	0,251	<LD
D20A – C_{16-18}	0,576	0,028	0,136	<LD
D20A – Amp	0,564	0,022	0,136	<LD
DAmp	0,538	0,008	2,177	<LD
* Detection limit for Hg (LD) is 4 ppb				

Both SR CR 13695-1: 2002 and GD nr.621/2005 and Directive 94/62/EC and amendments, set conditions on the management of packaging and packaging waste to prevent environmental impact. Therefore analysis of the content of heavy metals that are produced packaging materials, meets the essential requirements that will ensure a high level of environmental protection.

Mechanical properties analysis results

Table 5 Mechanical properties analysis

No	Sample	Tensile strength σ_r (MPa)	Elongation at break Al_r (%)
1	M (PEJD)	17,4	363
2	M1 (PEJD+MA)	11,7	313
3	D20A	14,0	175
4	D20A-QBR	12,3	81
5	D20A-$C0_8G$	12,4	123
6	D20A-C_{16-18}	12.2	200
7	D20A-Amp	11,4	152

Table 6 Tensile strength

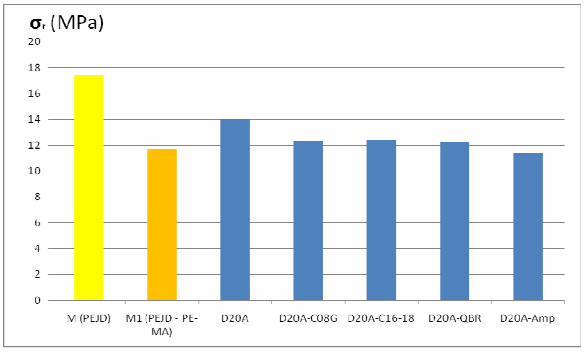
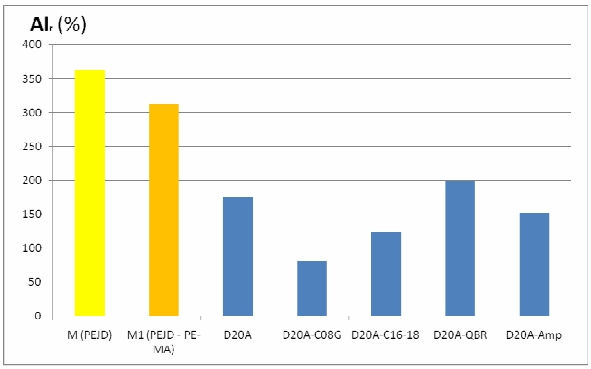


Table 7 Elongation at break



Nanocomposite films from D20A series containing modified silicate presents an improvement of tensile strength, and at the same time, a decrease of elongation, compared with control samples.

Morphostructural properties analysis results

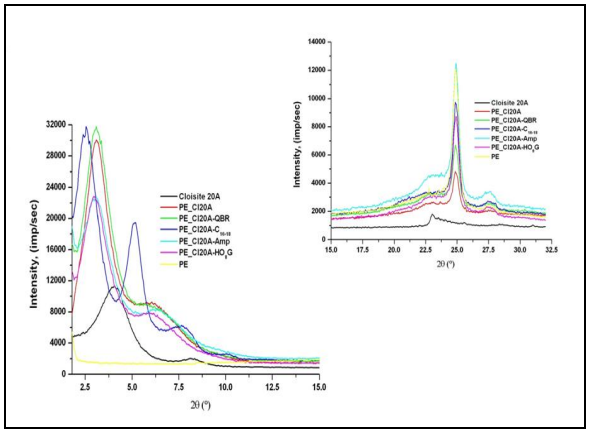


Figure 5 XRD analysis

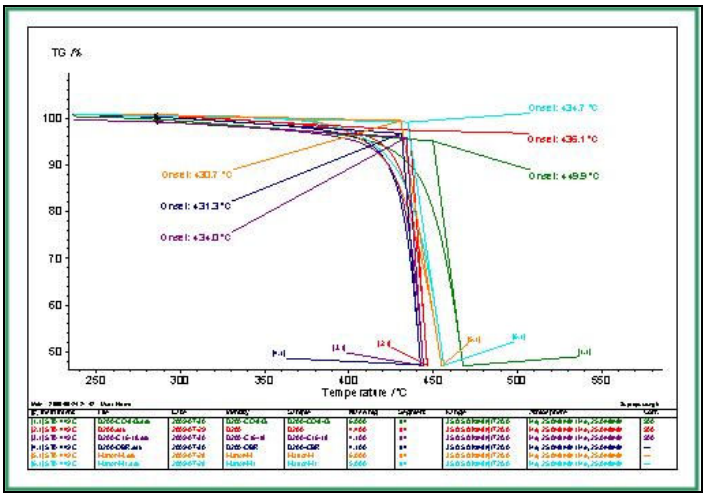


Figure 6 TGA analysis

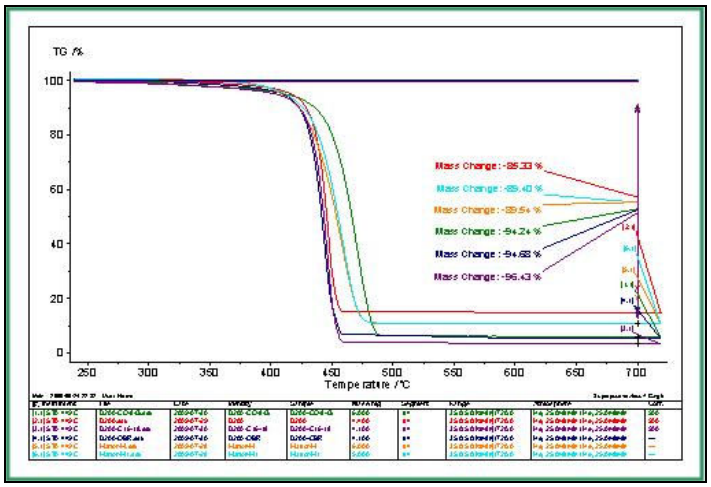


Figure 7 TGA analysis

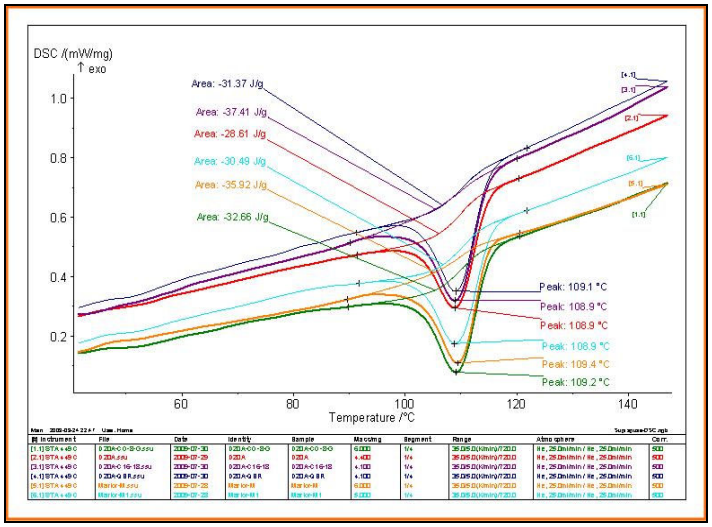


Figure 8 DSC analysis

The nanocomposites containing modified silicate with quebracho and C_{16-18} acids exhibit a thermal degradation similar to the pristine matrix and to the nanocomposite organofilized silicate.
The modification of the silicate with hydrolyzed collagen induces a higher thermal stability, the onset of degradation increasing by approx. 15°C.The supplemental modification of the silicate prevents the intercalation of the matrix between the silicate layers and limits or prevents the coke formation as the residue at 700°C of those nanocomposites is lower than that of the matrix. The extreme situation is presented by the C_{16-18} acids, the residue corresponding to the initial amount of inorganic content.

3. CONCLUSSIONS

Incorporating clay nano-particles in polymer had a very positive effect on water sensitivity problems associated with physical and mechanical stability of bio-plastic products;
Also, the incorporation of modified organophile silicate particles had the effect of improving the barrier properties to oxygen and water vapor necessary product packaging;

Results of heavy metals content analysis (lead, cadmium, total chromium, and mercury) of materials were evaluated according to both food contact and requirements of the environmental protection norms.
The test results will form the basis for the use of polymeric materials, for active packaging of foods and establishing relevant properties specific field of use.

4. ACKNOWLEDGEMENTS

The financial support of "Parteneriate" Program of National Management Program Centre, by means of project no. 71-029/ 2007 for achieving this contribution is gratefully acknowledged.

5. REFERENCES

[1] Ahvenainen, R., Novel Food Packaging Techniques, 2007, pag. 1;
[2] Jeon, H. G., Jung, H.T., Lee, S.W., Hudson, S.D., Polymer Bulletin, 41 (1998) 107;
[3] Vuluga, Z., Paven, H., Donescu, D., Mat. Plast., 39(1), 2002, 19.