Researches on Multilayer Films with Barrier and Antimicrobial Properties

DANIELA TEODORESCU[1], **CAMELIA HODOSAN**[2], **LUCICA NISTOR**[2], **GHEORGHE HUBCA**[3*]

[1] OSIM Bucharest, 5 Ion Ghica, 030044, Bucharest, Romania

[2] University of Agricultural Sciences and Veterinary Medicine Bucharest, Faculty of Animal Science, 59 Mărăşti, 011464, Bucharest, Romania

[3] Politehnica University of Bucharest, Department of Bioresources and Polymer Science, 149 Calea Victoriei, 010072, Bucharest, Romania

This paper has had as purpose rendering of some researches related to extrusion velocities while obtaining multilayer films with superior barrier and antimicrobial properties, of five layers of polymer with ionomer content, including antimicrobial. An installation comprising five extruders has been used for trials and the working velocities have been determined for each layer, as well as the shear stress at the wall of the nozzle. The results thus obtained made possible to settle the optimum parameters for the extrusion process able to ensure a stable flow of the molten polymer, which resulted in a uniform multilayer, faultless structural film, with superior barrier and antimicrobial effects.

Keywords: polyethylene, EVA, EVOH, extrusion, co-extrusion, multilayer film

Multilayer films are composite materials, obtained through co-extrusion, simultaneous lamination, cast or spray [1, 2]. Recently, a new method for obtaining multilayer films has been set, by assembling films of polymers (layer by layer), which is simple, robust and very versatile [3, 4].

Using these methods allowed obtaining films formed by 3 to 9 layers of different polymers, each contributing with different properties to the synergy of the final product (impermeability to liquids and gases, aromas, light, weldability, adherence to product etc).

Due to this aspect, multilayer films have found wide use as packaging in the food industry, medicine, cosmetics, being preferred against monolayer films that do not show such properties.

In recent decades more attractive are layers and multilayer films with barrier and antimicrobial properties, which have found uses in the food industry (packaging foils, boxes, containers for food [5-8]), but which have revolutionized the industry medical devices. On the basis of these materials, are obtained urinary catheters [9, 10], cardiovascular implants [11, 12], esophagus [13, 14], bandages [15-17] etc.

A concrete way of producing multilayer films with antimicrobial action is to incorporate substances containing halogen (especially Chlorine or Brom), being well-known their strong oxidative action and efficiency in destroying a wide range of microorganisms.

Although in most cases the chemical additives are highly effective, their action time is limited due to the migration phenomenon of composite material and possibilities of developing mutants resistant to their action.

These disadvantages have been eliminated by incorporating metal atoms or ions such as Ag [18-21], Cu [22-24], Zn [25-29] in the multilayer films.

The most active antibacterial agents are silver, copper or synergistic couples Ag-Cu [30].

There are several methods of incorporating the nano-particles of silver or silver ions in the composition of the multilayer film: placing the preformed particles of Ag, of colloidal silver, of Ag complexes with various substances, introduction of the Ag salts (eg $AgNO_3$) with the formation of particles silver in situ, production of LLDPE polymerized with catalyzed metallocenes, in presence of silver nano-powders [31-38].

The use of antimicrobial silver ions as additives in polymer formulations containing between 100ppm and 2500ppm increased worldwide by over 600% since 2001.

These ions may be added as antimicrobial additives in plastic materials such as those based on: polyolefins, polyvinyl chloride, ABS, polyurethane, polyamide, polymethyl methacrylate, polyethylene terephthalate [18-30].

Silver ions inactivate bacterial cells by penetrating the cells, preventing them from multiplying and causing their death. In contact with the silver ions, most bacteria are destroyed, starting from the low concentration of 1.25ppm for Haemophilus influenzae and Streptococcus pyogenes, to medium concentration of 5ppm for Staphylococcus aureus, and to higher concentrations of 10ppm for Candida albicans and Trichomonas vaginalis.

In consideration of the above, this paper aimed to obtain multilayer films, with barrier and antimicrobial properties. We have chosen for this purpose silver, zinc and manganese, as metals with potential antibacterial properties, which have been placed in the composite material in the form of ionomer.

As a particular processing method, we have chosen co-extrusion, process for which the working parameters have been determined, in order to obtain optimum uniform film, without structural defects.

Experimental part

Raw materials

In order to obtain multilayer films we used the following types of polymers as raw materials : Polyethylene linear low density polyethylene (LLDPE), ionomer of Mg (LLDPE+Mg), ionomer of Ag (LLDPE+1-octene+Ag),

* *email: gheorghe_hubca@yahoo.com; Tel.: 0744754210*

Polymer / Properties	LLDPE	LLDPE +Mg	LLDPE +Octene +Ag	LLDPE + Zn	PA6	EVA	EVOH	EMA-1	EMA-2
Density, (g/cm^3)	0.930	0.950	0.935	0.970	1.12	0.930	1.16	0.935	1.04
Tg*, °C	-125	24	-	-32	40	34.8	95	65	65
MFI**, 190°C, 2,16 kg [g/10 min]	0.3	1	-	4.0	-	2.0	2.0	12.0	5.15
Dynamic viscosity, 190°C, Pa·s x 10^{-3}	14.36	43.89	3.0	6.52	5.97***	21.55	16.83	3.603	9.25
Flow consistency coefficient, n (ec. 5)	0.60	0.40	0.60	0.65	0.70	0.40	0.45	0.45	0.45

Table 1
CHARACTERISTICS OF RAW MATERIALS USED TO OBTAIN MULTILAYER FILMS WITH BARRIER AND ANTIMICROBIAL PROPERTIES

Tg=glass transition temperature; MFI**=melt flow index ; ***-determined at 225°C*

ionomer with zinc (ZLLDPE+Zn), polyamide 6 (PA6), ethylene-vinyl acetate copolymer (EVA), ethylene-ethylene acrylate, one used as a surface modifier (EMA-1) and the second one used as anti-blocking agent (EMA-2).

The characteristics of these polymers are presented in table 1.

The equipment

Experimental determinations were made on an Omicron facility, equipped with five extruders [1,39]. The extruder head is similar with the head used and patented by Dr.Collin GmbH, DE 4115229/1991 and presented in one previous article [39].

Determination of optimal working parameters

Determination of dynamic viscosity

The Wiliams-Landel-Ferry model (WLF) [39-42] has been used for the dynamic viscosity calculus of polymers at different temperatures. This model has been expressed by the equation (1):

$$\eta(T) = \eta_0 \cdot \exp\left(\frac{-C_1 \cdot (T - T_r)}{C_2 + T - T_r}\right) \quad (1)$$

where:T-is the calculating temperature, °K, T_r-reference temperature, °K, C_1, C_2, - constants; when T_r equal T_g have the values $C_1H \approx 17.44$; $C_2H \approx 51.6$; η_0, η-initial and final viscosity.

Knowing the viscosity of the polymer melt at a first temperature determined by equation (1) and the glass transition temperature, the viscosity at a second temperature can be determined using the formula:

$$\frac{\eta(T2)}{\eta(T1)} = \frac{\exp\left(\frac{-C1 \cdot (T1 - Tg)}{C2 + T1 - Tg}\right)}{\exp\left(\frac{-C1 \cdot (T2 - Tg)}{C2 + T2 - Tg}\right)} \quad (2)$$

where:

T1-the first known temperature (°K); T2-the second temperature (°K), at which the viscosity is calculated; Tg-glass transition temperature of the polymer (°K), for which the viscosity is calculated.

Determination of the pressure drop, flow rate and shear stress at the nozzle wall

In order to determine the pressure and flowing velocity drops of every layer, it has been pre-estimated a material flow for every extruder and it has been taken into account the equation (3) of the pressure drop Δp at the nozzle wall with the relation [43]:

$$\Delta p = \left[\frac{Dv}{\pi R^3} \cdot \frac{3n+1}{n \cdot \dot{\gamma}^0}\right]^n \left(\frac{2\eta^0 \cdot \dot{\gamma}^0 \cdot L}{R}\right) \quad (3)$$

in which Δp – pressure drop, Pa; Dv – volumetric flow, m^3/s; R= 0.2 m – nozzle radius, η^0- dynamic viscosity, Pa.s ; γ^o-velocity gradient at the reference state, which in this case is $1s^{-1}$; L=0.035m – nozzle length,

With the obtained value for Δp from the equation (3) introduced in the equation (4) of the pressure drop as a velocity function,

$$\Delta p = \xi \frac{w^2}{2\dot{\gamma}^0} \rho \quad (4)$$

the flowing velocity has been determined corresponding to every layer with the equation (5) [43]:

$$w = \sqrt{\frac{2 \cdot \Delta p \cdot \dot{\gamma}^0}{\xi \cdot \rho}} \quad (5)$$

where: $\xi=1$, coefficient of local resistance for the case of fluids with sudden exstress; ρ = density of material, kg/m^3.

The average velocity in the middle plane, which in fact is a correction of the flowing velocity, on every extruder, has been calculated with the relation (6)[43]:

$$w_m = \left(\frac{n+1}{2n+1}\right) w \qquad (6)$$

where n has the following values [44-45] :
for LDPE 0.35; for EVA 0.40; for EMA 0.40, for EVOH 0.45, for LLDPE 0.60 and for PA6 0.70.

The shear stress at the nozzle wall τ, in Pa, is calculated with the expression (7) [43]:

$$\tau = \frac{\Delta p}{2\left(\frac{L}{r}\right)} \qquad (7)$$

where: L=0.035 m-nozzle length r=0.2 m-nozzle radius.

Three types of multilayer films of the following compositions have been taken into consideration:

a) 31.25%LLDPE/6.25%EVA/25%PA6/6.25%EVA/31.25% (29.25%LLDPE+2% Mg) corresponding to the thickness of 50/10/40/10/50 mm, which by co-extrusion gives a total thickness of 160 mm.

b) 18.57%LLDPE/13.60%(9.60%LLDPE+4%EMA)/17.60%LLDPE/13.60%

(9.60%LLDPE+4%EMA)/36.64% Ionomer (with 2%Zn), corresponding to the thickness of 18/12/18/12/40 mm, which by co-extrusion gives a total thickness of 100 mm.

c) 33.68% LLDPE+0.4%Ag (with pre-compound of LLDPE+1-octene with 0.4%Ag/ 11.58%(9.58% PA6+2%EVOH)/28.42% Ionomer (with 2%Zn), corresponding to the thickness of 32/11/14/11/27 mm, which by co-extrusion gives a total thickness of 95 mm.

The results obtained are given in tables 2-4.

Results and discussions

a) Determination of speeds for multilayer film LLDPE+Mg/EVA/PA6/EVA/ LLDPE with final width of 810 mm.

The following characteristics of used polymers were considered:

LLDPE: $\rho=920kg/m^3$, $\eta=3x10^4Pas$, n=0,60; EVA: $\rho=930kg/m^3$, $\eta=28.57x10^3Pas$, n=0,40;

PA6:$\rho=1120kg/m^3$, $\eta=35.7x10^3Pas$, n=0.70; Extrusion head :$\rho_{am}=972$ kg/m^3, n=0.55, η_{am} = $32x10^3Pas$.

The results obtained are presented in tables 2-4.

Working parameters	Exterior layer	Adhesive Layer 1	Central Layer	Adhesive Layer 2	Interior Layer	Extrusion head
	LLDPE+Mg	EVA	PA6	EVA	LLDPE	
Suggested thicknesses of film, µm	50	10	40	10	50	160
Accomplished thickness, µm	49.3	10.2	39.7	11.0	49.4	159.6
Pressure, kgf/cm^2; MPa	156 15.3	175 17.1	405 40.2	135 13.2	308 30.2	310
Melt temperature, °C	210	210	225	220	190	235
Current Intensity, A	28	29	79	45	70	0.5
Screw velocities, rot/min	23	23	57	89	62	65
Flow, kg/h	60	12	48	12	60	192
Flow, m^3/s x 10^5	$1.8 \cdot 10^{-5}$	0.36	1.12	0.36	1.8	5.48
Viscosity, Pa·s x 10^{-3}	21.1	14.68	5.97	12.39	30	21.1
Density, kg/m^3	920	930	1120	930	920	972
Index of flow consistency from ec.(5) n, dimensionless	0.60	0.40	0.70	0,40	0.60	0.54
Pressure drop, Pa	241.42	294.69	152.64	248.72	343.25	602.74
Speed, m/s	0.72	0.79	0.52	0.73	0.86	1.11
Corrected speed, m/s	0.52	0.61	0.37	0.57	0.62	0.82
Shear stress at nozzle wall, MPa x 10^3	0.377	-	-	-	-	0.377

Table 2
THE WORKING PARAMETERS TO OBTAIN THE STRUCTURE OF FILM LLDPE/EVA/PA6/EVA/LLDPE

Working parameters	Exterior layer	Adhesive Layer 1	Central Layer	Adhesive Layer 2	Interior Layer	Extrusion head
Material	LLDPE	LLDPE+EMA	LLDPE	LLDPE+EMA	Ionomer with Zn	
Thicknesses of film, µm	16	13	18	13	40	100
Accomplished thickness ,mm	16.9	12.76	17.9	12.9	40.5	100.96
Pressures, kgf/cm^2	240	242	240	220	242	200
Melt temperature, °C	232	235	238	239	237	240
Current intensity, A	43	44	67	51	77	0,5
Screw velocities, rot/min	40	61	48	61	57	-
Flow, kg/h	19	17	22	17	50	125
Flow, m3/s	$5.7.10^{-6}$	$5.1.10^{-6}$	$6.6.10^{-6}$	$5.1.10^{-6}$	$1.43.10^{-5}$	$3.73.10^{-5}$
Speed, m/s	0.53	0.48	0.64	0.48	0.98	0.93
Corrected speed, m/s	0.39	0.35	0.46	0.35	0.70	0.67
Sheer stress at nozzle wall, MPa x 10^3	0.981					0.981

Table 3
THE WORKING PARAMETERS TO OBTAIN THE STRUCTURE OF FILM : LLDPE/LLDPE+EMA/ LLDPE/LLDPE+EMA/IONOMER

b) Determination of speeds for the multilayer film with the structure LLDPE/LLDPE+EMA/LLDPE/LLDPE+EMA/ IONOMER with Zn, width of 800 mm.

The following characteristics of used polymers were considered:

LLDPE: $\rho = 920 kg/m^3$, $\eta = 3x10^4 Pas$, $n = 0,60$; LLDPE+EMA: $\rho = 925 kg/m^3$, $\eta = 2x10^4 Pas$, $n = 0.40$; Ionomer cu Zn: $\rho = 970 kg/m^3$, $\eta = 6.52x10^4 Pas$, $n = 0.65$; Extrusion head : $\rho_{am} = 932 kg/m^3$, $n = 0.65$, $\eta_{am} = 3.2x10^4 Pas$

c) Determination of speeds for the multilayer film with the structure LLDPE+1-OCTENE (with 0.4%Ag)/PA6 (with 2%EVOH)/ LLDPE /PA6(with 2% EVOH)/Ionomer (with 2%Zn) final width of 1100 mm.

The following characteristics of used polymers were considered:

LLDPE+1-OCTENE+AG: $\rho = 935 kg/m^3$, $\eta = 3.1x10^4 Pas$, $n = 0.60$; LLDPE: $\rho = 920 kg/m^3$, $\eta = 3x10^4 Pas$ PA6+EVOH: $\rho = 1140 kg/m^3$, $\eta = 35.7x10^3 Pas$, $n = 0.70$; Ionomer with Zn: $\rho = 970 kg/m^3$, $\eta = 3.1x10^4 Pas$, $n = 0.70$; Extrusion head : $\rho_{am} = 1020 kg/m^3$, $n = 0.65$, $\eta_{am} = 32x10^3 Pas$,

The working parameters to obtain the multilayer films with structure LLDPE+1-OCTENE+Ag/PA6+EVOH/ LLDPE/PA6+EVOH/IONOMER are presented in table 4.

The analysis of the data from tables 2-4 showed the following:

- the flow rates recorded for the multilayer films with ionomer based on zinc in the outer layer are higher than those for films with magnesium-based ionomer in the outer layer (0.70 m / s versus 0.52 m / s);
- for PA6, the flow rate is 0.37 m / s versus 0.43 m / s for PA6 + EVOH;
- the flow rate for the ionomer with Ag is the same or very close to the flow rate of the other layers, which is a guarantee for obtaining multilayer films with appropriate properties;
- shear stress at the nozzle wall is very close to zero, leading to easy flow of the polymer through the nozzle, the values of the shear stress being below the critical shear stress of the polymers, as given in the special literature.

For the incorporated silver foil, physico-mechanical characteristics were determined and the results are shown in table 5.

In order to obtain uniform antimicrobial properties in all parts of the multilayer film, the distribution of silver ions in the polymeric material is very important.

In order to obtain information related to the distribution of silver ions in the composite, the SEM spectra were recorded using a Scanning Electron Microscope apparatus.

Working parameters	Exterior layer	Adhesive Layer 1	Central Layer	Adhesive Layer 2	Interior Layer	Extrusion head
Material	LLDPE+ 1-octene+0,4% Ag (premix with LLDPE)	PA6+ EVOH	LLDPE	PA6+ EVOH	Ionomer with Zn	
Thicknesses of film, μm	32.00	11.00	14.00	11.00	27.00	95 μ
Accomplished thickness, mm	31.6	11.4	14.6	11.6	27.3	96.5 μ
Pressures, kgf/cm2	240	242	246	242	235	220
Melt temperature, °C	233	235	225	235	230	240
Current intensity, A	40	55	50	55	52	0,5
Screw velocities, rot/min	38	50	48	50	47	-
Flow, kg/h	38.4	13.2	16.8	13.2	32.4	114
Flow, m3/s	$1.14x10^{-5}$	$4.26x10^{-6}$	$5.8x10^{-6}$	$4.26x10^{-6}$	$9.28x10^{-6}$	$3.1x10^{-5}$
Speed, m/s	0.76	0.61	0.61	0.61	0.70	0.87
Corrected speed, m/s	0.43	0.43	0.45	0.43	0.51	0.62
Sheer stress at nozzle wall, MPa x 10^3	-	-	-	-	0.4813	

Table 4
THE WORKING PARAMETERS TO OBTAIN MULTILAYER FILMS WITH THE STRUCTURE LLDPE+1-OCTENE+Ag/ PA6+EVOH/LLDPE/PA6+EVOH/ IONOMER Zn

	Determined characteristics	UM	Testing method	Minimum Values as guidance for use, compared to the majority materials	Achieved Values
1	Traction (pulling speed 100mm/min) MD-tensile strenght - tension - elongation	 Kgf/cm^2 %	 ISO 1184 :83	 min 255.5 -	 275 10
	-to tear - resistence - elongation	 Kgf/cm^2 %		 min 265 200	 260 250
	TD-in tension - tension - elongation	 Kgf/cm^2 %		 min 61.18 -	 118.30 8
	-to tear - resistence - elongation	 Kgf/cm^2 %		 102 250	 140 250

Table 5
THE PHYSICO-MECHANICAL PROPERTIES OF MULTILAYER FILM WITH INCORPORATED SILVER

2.	Resistence at shock by Traction MD- for sheet -for material	 J/m J/m	ISO 6526, sample type 2 şi 3	 - -	 110 105
3.	TD- for sheet - for material	 N J	ISO 7765-2	 min 50 -	 55 0.43
4.	Resistence to impact Dartvis, multiaxially - impact strength to tear	N	ISO 6383-2	-	19
	- impact energy to tear	N		-	22
5.	Resistence at laceration MD -for sheet - for material	$cm^3/m^2/24h$	ISO 2556 :74	-	3
6.	TD-for sheet -for material	$g/m^2/24h$		max 4	3.6
7.	Permeability at oxygen (23°C, 1 bar)	g/m^2	ISO 4591:92		118

Table 5

Images obtained by scanning electronic microscopy (SEM) of the multilayer films with incorporated silver are shown in figure 1 and 2.

The analysis of SEM images shown in figure 1 and 2 reveals a fairly uniform distribution (no lumps) in the multilayer film, which will ensure sterilization for the products stored in packaging made of this composite material.

In order to verify the antimicrobial properties of the multilayer films with silver incorporated, cytotoxicity assays were carried out "*in vitro*".

The biological properties in terms of cytotoxicity and cyto-compatibility tests have been studied through "in vitro" tests, with cell culture method. The toxicology test was performed according to ISO 10993-1, Biological Evaluation of Medical Devices Part 1: Guidance on selection of test and STAS 10914-89.

"*In vitro*" biocompatibility tests were conducted on lines of epithelial cell using the technique of cell growth in suspension. The test was run on fibroblasts, monkey kidney epithelial cells in culture medium containing 10 % Dumeni fetal bovine serum and a mixture of three antibiotics (penicillin, streptomycin and neomycin). At least three test pieces of size 20x5 mm were sterilized by exposure to UV for 8 h. Three such samples were put in 2 mL cell suspension, placed in Petri culture dishes. Incubation took place at 37°C for 3 to 6 days . The culture medium was changed every 3 days. Samples were examined daily with an optical microscope at a magnification of 160X , 250X and 400X. Visual examination of the evidence in the form of films was made with an IOR Bucharest Romania microscope. For histological examination, the samples were treated with a Bouin buffer, dehydrated with ethanol and stained "*in toto*" using van Gieson method. Microscopic

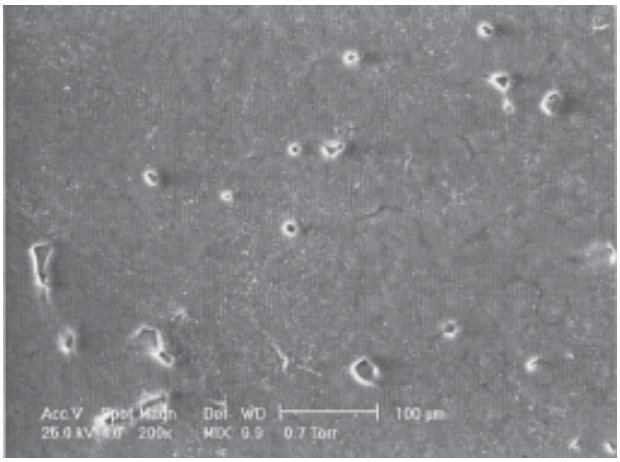

Fig.1. SEM microscopy of the multilayer film with incorporated silver

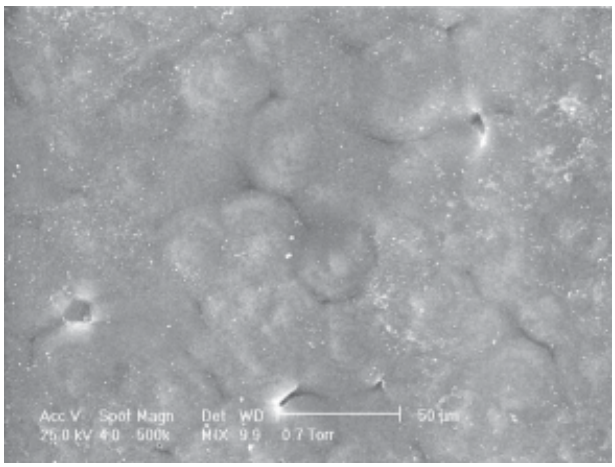

Fig.2. SEM microscopy of the multilayer film with incorporated silver

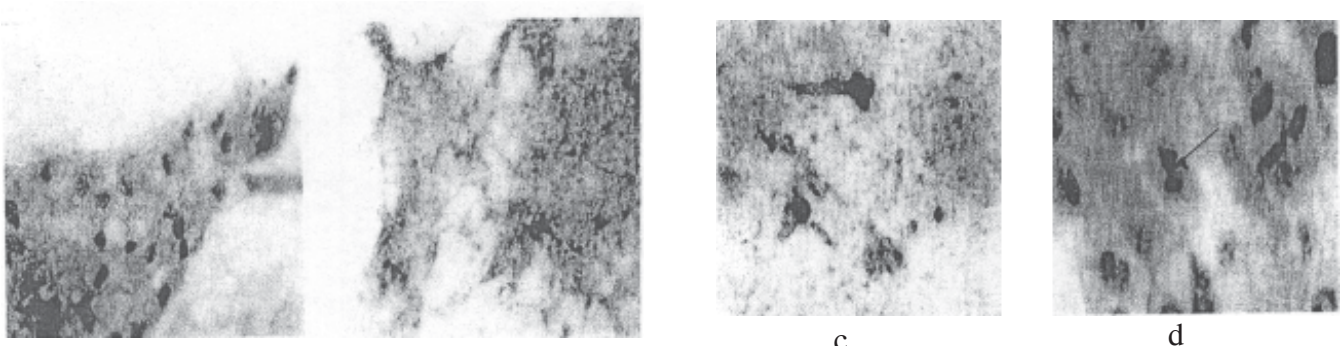

Fig. 3. Optical microscopy images of a sample of film with incorporated silver kept in the culture of epithelial cells for 96 h

images were compared, rating with notes the behaviour under test conditions.

After testing "*in vitro*" samples of multilayer film, it was observed that, after 24 h, the samples did not have cytostatic effect on cell culture. In addition, cells exhibited cell phenomenon of adherence at the surface of all the samples studied.

After 48 or 72 h of maintenance in cell culture, no alterations were observed in cells which have been contacted with the test materials.

Optical microscopy images of the mixture of multilayer films kept in the culture of epithelial cells for 96 h demonstrated that they were arranged in a monolayer on the surface of the sample (fig. 3a). This monolayer is expanding because the ends of the cells continues to occupy vacant spaces (fig. 3b). It is also observed that on the polymer surface are isolated cells or small groups of cells (fig. 3c). From the morphological point of view, the cells are flattened on the substrate and generally fusiform. Their nuclei are round or oval, with granular chromatin 1-2 distinct nucleoli, while others are in division (fig. 3d).

Conclusions

The flow rates of the ionomers differ one from another depending on the ionomer, the working pressure and the speed of the screw.

The shear stress of the polymers without metal ions at the nozzle wall are higher than the shear stresses of ionomers, but are within the range of values very close to zero, but below the critical value, which facilitates free flow without fracture of melt phenomena.

The SEM analysis of multilayer films obtained showed that the dispersion of silver particles is fairly uniform to ensure sterilization of the products that come in contact with it, concluding that the materials obtained can be used to obtain goods or packaging biocompatible for use in food, medical or cosmetic industry.

"*In vitro*" tests on samples of multilayer film with incorporated silver highlighted their antimicrobial properties.

References

1. STĂNESCU, P.O., TEODORESCU, D., HUBCA, Gh., Ambalaje polimerice pentru produse alimentare, Ed. MATRIX ROM, Bucureşti, 2010, p. 271.
2. SANCHEZ-VALDES, S., ORTEGA-ORTIZ, H., RAMOS-DE VALLE, L.F., MEDELIN-RODRIGUEZ, F.J., J. Appl. Polym. Sci. **111**, 2009, p. 953.
3. DECHER, G., Science, 277, 1997, p. 12327.
4. ZHANG, X., CHEN, H., ZHANG, H.Y., Chem. Comm., 2007, 1395.
5. KOUNOSU, M., KENEKO, S., Biocontrol. Sci., **12**, 2007, p. 123.
6. BERRANG, M.E., FRANK, J.F., MEINERSMANN, R.J., Food Prot. Trends, **30**, 2010, p. 168.
7. QUITAVALLA, S., VICINI, L., Meat Sci., **62**, 2002, p. 373.
8. APPENDINI, P., HOTCHKISS, J.H., Innovative Food Sci., Emerging Technol. **3**, 2002, p. 113.
9. SAINT, S., ELMORE, J.G., SULLIVAN, S.D., EMERSON, S.S., KOEPSELL, T.D., Am.J.Med. **105**, 1998, p. 236.
10. LOETZER, H., SOUKUR, J., HAMZA, A., WICHT, A., KOCH, E., FORNARA, P., Transplant Proc. **38**, 2006, p. 707.
11. RICCO, J.-B., J.Vasc. SURG., **44**, 2006, p. 339.
12. GUGENBICHLER, J.-P., KRALL, T., Infection, 27, 1999, p. 16.
13. KOLLET, M.H., AFESSA, B., ANZUETO, A., VEREMAKIS, C., J. Am.Med.Assoc. **300**, 2008, p. 805.
14. OLSON, M.E., HARMON, B.G., KOLLET, M.H., Chest, **121**, 2002, 863.
15. WRIGHT, J.B., LAM, K., BURREL, R.E., Am.J.Infect. Control **26**, 1998, p. 572.
16. CHU, C.-S., MATYLEVITCH, N.P., Mc MANUS, A.T., GOODWIN, C.W., PRUIT, B.A., TRAUMA, J., Inj. Infect Crit. Care, **49**, 1999, p. 1371.
17. BLAKER, J.J., NAZHAT, S.N., BOCCACINI, A.R., Biomaterials, **25**, 2004, p. 1319.
18. TANKHIWALE, R., BAJPAI, S.K., Colloids. Surf., B69, 2009, p. 164.
19. HONG, K.H., PARU, J.L., SUL, I.H., YOUK, J.H., KANG, T.J., J. Polym. Sci., Part B: Polym. Phys., **44**, 2006, p. 2468.
20. KONG, H., JANG, J., Langmuir **24**, 2008, p. 2051.
21. SHEIKH, F.A., BARACAT, N.A.M., JUNG, I.H., LEE, J.H., KIM, H.Y., Macromol. Res. 17, 2009, p. 688.
22.YOON, K.-Y., BYEON, J.H., PARK, J.H., HWANG, J., Sci. Total Envirom. **373**, 2007, p. 4419.
23. MARY, G., BAJPAI, S.K., CHAND, N., J. Appl. Polym. Sci., 113, 2009, p. 757.
24. CARDENAS, G., DIAZ, J., MELENDREZ, M., CRUZAT, C., CANCINO, A.G., Polym. Bull. **62**, 2009, p. 511.
25. XIE, Y., HE., Y., IRWIN, P.L., JIN, T., SHI, X., Appl. Envirom. Microbiol. **77**, 2011, p. 2325.
26. JIN, T., SUN, D., SU, J.Y., ZHANG, H., SUE, H.-J., J. Food. Sci., **74**, 2009, p. M46.
27. LIU, Y., HE, L., MUSTAPHA, A., LI, H., HU, Z.Q. LIN, M., J. Appl. Envirom. Microbiol. **107**, 2009, p. 1193.
28. SEVINC, B.A., HANLEY, I., J. Biomed. Mater. Res. Part B **94**, 2010, p. 22.
29. LEE, S., J. Appl. Polym. Sci., **114**, 2009, p. 3562.
30. Mc LEAN, R.J.C., HUSSAIN, A.A., SAYER, M., VINCENT, P.J., Canadian Journal of Microbiology, **39**(9), 1993, p. 895.
31. ZAN, X., SU, Z., Thin solid Films, **518**, 2010, p. 5478.
32. GAO, S., Wu, Z., PAN, D., LIN, Z., CAO, R., Thin Solid Films, **519**, 2011, p. 2317.
33. DECHER, G., SCHLENOFF, Multilayer Thin Films: Sequentical Assembly of Nanocomposite Materials, Second ed., Wiley-VCH, Weinheim, Germany, 2012, p. 1046, ISBN 978-3-527-31648-9.
34. ANANDHAKUMAR, S., RAICHUR, A.M., Acta Biomaterialia, **9**(11), 2013, p. 8864.

35. RATCHANEE, C., APISIT, K., NARONGRIT, S., J. of Plastic Film and Sheeting, 29(2), 2013, p. 2144.
36. FU, J., JI, J., FAN, D., SHEN, J., J. Biomed. Res. **79A**, 2006, p. 665.
37. SANCHEZ-VALDES, S., ORTEGA-ORTIZ, H., RAMOS-DE VALLE, L.F., J. Appl. Polym Sci., 111, 2009, p. 953.
38. DUNCAN, T.V., J. Colloid. Interface Sci., 2011, doi: 10.1016/J. jcis. 2011.07.017.
39. TEODORESCU, D., JINESCU, V.V., HODOŞAN, C., HUBCA, Gh., CINCU, C., Mat. Plast. **51**, no. 1, 2014, p. 37.
40. ODIAN, G., Principles of Polymerization, Wiley Interscience, 2004, p. 31.
41. MARK, J., Physical properties of Polymer Handbook, Second ed., Springer, U.S., 2003, p. 99.
42. LIDE, D., FOX, R., CRC Handbook of Chemistry and Physics-teen LRN, Glass Transition Temperature for Selected Polymers, 2007-2009, p. 13-14.
43. CHUNG, C.-I., Extruzion of polymers: theory and practice, Hanser Ed., U.S., 2000, p. 142.
44. HARRIS, R.M., Coloring technology for plastic, Plastics Design Library, Ed. William Andrew Inc., U.S. 1999, p. 158.
45. RAUVENDAAL, C., Polymer Extrusion, Revised, 4th Edition, Hanser, 2001, p. 335.
46. KALYON, D.M., GEVGILILI, H., Wall slip and extrudate distorsion of three polymers melt- Stevens Institute of Technology , New Jersey, 7 Jan 2003, p.684.
47. KALYAN, D. M., BIRINCI, E., GEVGILILI, H., Developement of Extrusion Instabilities and surface irregularities, Stevens Institute of Rheology, US, 2003, p. 2-37, 11-15, 75.

Manuscript received: 12.03.2014