Research on Obtaining Polyolefin Composites with Embedded Silver for Synthesis Hollow Bodies with Antibacterial Properties

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This paper is about obtaining polyolefin composites with antibacterial properties for the manufacture of hollow blown bodies (vials, bottles, jars) used for the packaging of medical products, cosmetics and food. As main polymer, it was used polypropylene, and as biocide active agent, it was used silver chloride deposited on a support of titanium dioxide or of silica. Antimicrobial silver was added as a premix, using for this purpose the co-polymer ethylene-1-octene. Hollow bodies were obtained by extrusion-blowing and were tested for their mechanical properties and biocompatibility.

Keywords: polypropylene, co-(ethylene-1-octene), hollow blown bodies, extrusion

In recent decades, worldwide, it was observed a particular interest in obtaining medical devices (catheters, tubes, endotracheal tubes, cannulae, enteric feeding tubes, dental prostheses and implants) and packaging (bottles, jars, containers) with antibacterial properties.

Among these products, an important role is played by antibacterial hollow bodies. Antimicrobial character can be inoculated by incorporating in the polyolefin composites of natural antimicrobial agents (such as antimicrobial peptide nisin, pediocin, enterocin, lacticin), of organic acids, their salts and anhydrides, enzyme (ex. lysozyme) or chemical agents such as metals or combinations thereof based on silver, copper and zinc [1,2].

The most effective chemical antibacterial agents are compounds containing silver ions or silver nano-particles [3,4].

Silver ions present the highest efficiency, but they have poor stability in polymer composites due to the possibility of their reduction to metallic silver, which reduces the duration and antibacterial action.

Deposition of AgCl or $AgNO_3$ on inert media such as titanium dioxide or silica increases the stability of silver ions [5-7].

If silver is present in metallic or oxide form it is stable, but, in order to obtain adequate antimicrobial activity, large quantities are required. The most used in antimicrobial compositions are silver nanoparticles, usually placed on oxides or hydroxides of titanium or tantalum.[8].

In order to obtain silver nano-particles, there have been developed several methods: chemical reduction of the silver ions in the presence of a stabilizing agent [9-13], thermal decomposition of organic solvents [14, 15], electrochemical methods [16], sonochemical [17], photochemical [18,19], synthesis in microwave field [20, 21], radiation-assisted processes [22,23] and methods based on green chemistry [24-27]

Incorporation of silver ions and nano-particles in polymer composites causes great effects both on fungi (*Candida spp Cryptocroccus spp, Aspergillus spp, Trichophyton spp, Chaetomium spp,* etc.) and on bacteria (*Escherichia, Bacillus, Pseudomonas, Chetonium, Staphylococcus, Klebsiella, Legionella, Salmonella, Vibrio and Ricketsia*) [2].

Antibacterial activity of the silver ions or silver nano-particles is much discussed in literature. It is believed that silver ions react with the groups electron-donators (atoms N, O or S) which are present in the bacteria: the amino, imidazole, phosphate, carboxyl or thiol [28-30].

In this paper for obtaining hollow bodies with antibacterial properties silver chloride deposited on titanium dioxide or silica has been used.

Experimental part

Raw materials

The polymers used for obtaining hollow bodies are antibacterial polypropylene, ethylene-1-octene copolymer and ethylene-vinyl acetate copolymer (EVA). The characteristics of these polymers are shown in table 1.

Property / Polymer	Polypropilene	Ethylene-1-octene Copolymer	EVA Copolymer
Density , g/cm^3	0.905	0.902	0.930
Tg*, °C	-18	-24	-34.8
MFI**, 190°C, 2,16kg, g/10min	0.2	0.7	2.5
Dynamical Viscosity, 190°C,Pa·s·10^{-3}	1.02	3.0	2.155
Power law Index, n	0.41	0.60	0.40

Table 1
PROPERTIES OF POLYMERS USED FOR OBTAINING HOLLOW BODIES

Neo alcoxi zirconate [$(RO)_n - Zr(OxR=Y)_{4-n}$] or alcoxi titanate [$(RO)_n - Ti(Ox\ R=Y)_{4-n}$] type Ken React NZ, produced by Kenrich SUA have been used as modifiers of intra-molecular structure.

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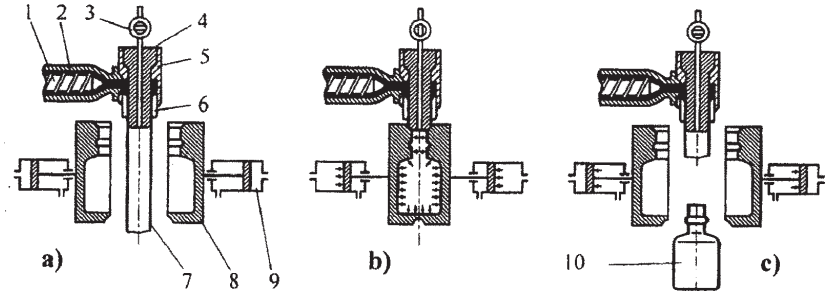

1. Process diagram for obtaining hollow bodies through extrusion-blowing
a)-obtaining the pre-form tube;
b)- blowing the pre-form and obtaining the finished product; c)- remove of finished part [31]
1- snail, 2- molten polymer, 3- inlet valve for compressed air, 4- mandrel, 5- square unit, 6- nozzle (pathway), 7- pre-form tube, 8- half-mould, 9- actuator of half-moulds, 10- finished product

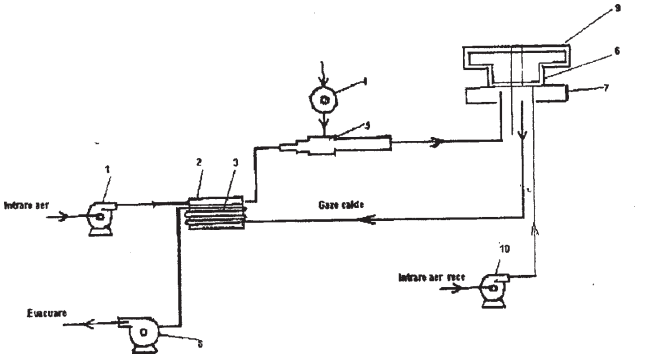

Fig.2. Installation for extrusion-blowing of hollow bodies and vials [34,35]. 1. Blower air intake, 2. Humidifier with water, 3. Heat exchanger-evaporator, 4. Compressor, 5. Ejector, 6. Extruder, 7. Blowing head and forming mould, 8. Blower outlet, 9. Forming mould

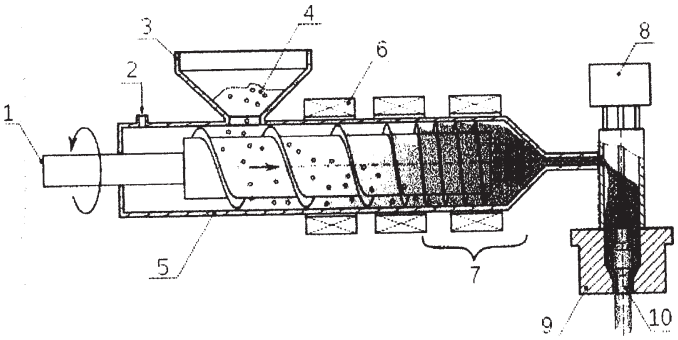

Fig. 3. Diagram of the extruder used for obtaining hollow bodies [36,37]. 1. –axis of extruder, 2-compressed air intake, 3-inlet hopper, 4- granules of polymer, 5- cylinder of extruder, 6- heating system, 7- mixing zone, 8- hydraulic group, 9- pathway, 10- piercer

As clarifying agent it was used bis(3,4-dimetilbenziliden) sorbitol (from Waterstone Technology LLC), as antioxidant it was used 2,2'-methylene-bis-(4-methyl-6-tert-butyl phenol) (from KOWA EUROPE GmbH), as stabilizer it was used triizodecil phosphite (from Sigma Aldrich) and as de-acidification agent, calcium stearate (from Sigma Aldrich).

Equipment and work procedure

To obtain hollow bodies it was used the extrusion-blowing process.

The principle of the method consists in the continuous flow of a polymer, plasticized and homogenized, in an extruder operating in flow direction (parallel) or vertical blank in the form of a tube. The tube is inserted between the jaws of a mould, defining the outer contour of the desired product. The mould then closes, closing also the cut end of the tube, after which air is blown inside it. Polymer tube, which is viscous in the plastic state, is expanded to contact the mould walls, cooling (fig. 1) [31-33].

Diagram of extrusion-blowing installation used in this study is shown in figure 2 [34,35].

It was used to produce hollow bodies through extrusion in an Polyflex, Inc. origin. whose diagram is shown in figure 3 [36,37].

The work procedure was the following.

The mixture of granules is fed into the basket of the extruder from where it is picked up, through free fall, by the extruder and plasticized at a temperature which gradually increases from 180 to 250° C and fed through the head of accumulation in the forming mould, cooled from the outside with 15-20° C water. In the mould, the melt tube is inflated until touching the mould walls and hence the shape of the final product, cooled by air flow, from water vapour and particulate matter, mists pressurized by the joint action of which the walls of the mould leads to the adoption of the form mould and cooling requirements of the vial at ambient temperature, followed by evacuation, and resumption of the cycle of the product.

The air laden with water, or fog, is achieved by passing air through the air conditioners and the cooling is achieved by injection, at a pressure of 7atm, of air from compressor 4 and further fed to ejector 5 inside the molten polymer tube into the mould, accomplishing the making and final cooling of the hollow body on account of the heating and evaporation of the water coolant.

The hot gases are discharged into the atmosphere via the heat exchanger which generates steam required for humidification.

For obtaining hollow bodies with antimicrobial characteristics with double or triple layer a co-extruder was used, the system being equipped with an extrusion head with individual inlet channels for each polymer and, in this case, with 3 inlet channels (fig. 4).

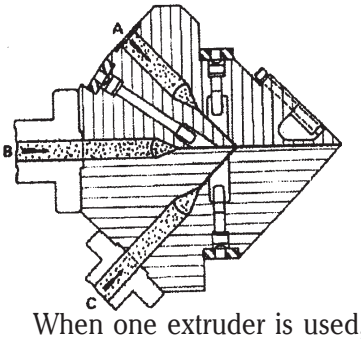

Fig.4. Extrusion head with individual inlet channels [31]

When one extruder is used, co-polymer ethylene-1-octene containing antibacterial agent is mixed with the polypropylene.

If it is desired that the antibacterial agent is introduced only into the inner layer, then the co-extrusion process will be used. In this case, the temperature regime, both for the main extruder and the co-extruder, for each area, is: 180/200/240/270/290°C, so that to provide a melt temperature of 280°C.

Hollow bodies obtained are tested for mechanical properties and biocompatibility.

The biological properties in terms of cytotoxicity and compatibility have been studied through "in vitro" tests, using cell culture method. The toxicological test was carried out according to standard ISO-10993-1, Biological

Components	Sample no.			
	1	2	3	4
Polypropilene	99.96	80	80	80
Ethylene-1-octene copolymer	-	20	20	20
LLDPE/ antibacterial agent Premix	-	-	0.3*	0.3**
3,4-dimethyldibenzylidene sorbitol	-	0.05	0.05	0.05
Structurally modifier	-	6.0	6.0	6.0
Antioxidant	0.015	0.015	0.015	0.015
Thermal stabilizer	0.010	0.010	0.010	0.010
Calcium Stearate	0.015	0.015	0.015	0.015
Pigmentation agents	0.015	0.015	0.015	0.015
EVA Copolymer	-	0.3	0.3	0.3

Table 2
COMPOSITION OF TESTED SAMPLES (MASS PARTS)

**- antimicrobial agent $AgCl/TiO_2$ (1/5 in mass)*
***- antimicrobial agent AgCl/Silice (1/5 in mass)*

PROPERTY	U.M.	P1	P2	P3	P4	Obs.
Opacity	%	62	22	23	26	-
Izod impact strength	J/m	50	55	56	52	ISO2818
Flexural strength	MPa	42	44	46	46.8	ISO527-2
Flexural Module	GPa	1.50	1.78	1.80	1.72	ISO527-2
Tensile strength	MPa	33	34,6	37,8	38,4	ISO527-1
Tensile module	MPa	1.15	1.28	1.36	1.47	ISO527-2

Table 3
PHYSICO-MECHANICAL PROPERTIES OF THE HOLLOW BODIES

Evaluation of Medical Devices Part I: Guidance on selection of tests and the standard STAS 10914-89.

Biocompatibility test "in vitro" was conducted on lines of epithelial cells, using the technique of cell growth in suspension. The test was conducted on fibroblasts with monkey kidney epithelial cells in DUMEN culture medium containing 10% human foetus serum and a mixture of three antibiotics (penicillin, streptomycin and neomycin). At least three test pieces of 20x5 mm size were sterilized by exposure to UV for 8 h. Three such samples were placed in 2 mL of cell suspension placed in Petri culture dishes. Incubation took place at 37 for 3 to 6 days. The culture medium was changed every 3 days. Samples were examined daily with a microscope magnification of 160X, 250X and 400X. Visual examination of the samples was done with a microscope IOR Bucharest Romania. For histological examination, the samples were treated with Boudin buffer Type, dehydrated with ethanol and stained "*in toto*" using von Gieson method. Microscopic images were compared, appreciating in notes the behaviour under test.

Results and discussions

In order to have terms of comparison, there were obtained polypropylene hollow bodies without additives, from composite material without antimicrobial agent and from composites with antimicrobial agent the silver chloride deposited on titanium dioxide or silica. The compositions tested are shown in table 2.

Out of the compositions shown in table 2, there were obtained hollow bodies as shown in figure 5.

The bodies obtained from compositions 2-4 had three layers (PP/EVA/Co-polymer ethene-1-octene), the inner layer of the samples 3 and 4 incorporating an antimicrobial agent.

From the walls of the hollow bodies obtained test pieces were cut and were subject to physico-mechanical measurements and bioavailability.

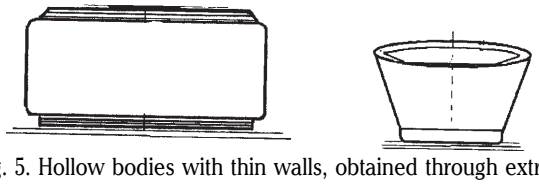

Fig. 5. Hollow bodies with thin walls, obtained through extrusion-blowing

The physico-mechanical properties of the hollow bodies obtained are shown in table 3.

Analysis of the data presented in table 3 reveals that the introduction of antimicrobial agents plays a role in reinforcing, the mechanical properties of components obtained being superior to those of native polypropylene.

With respect to biocompatibility test, the samples were characterized in terms of cytotoxicity compared to the negative control (A1), a PVC formulation for medical use (A2) and cytotoxic positive control, the receipt of PVC stabilized with an organometallic compound (A5).

The results are shown in figure 6.

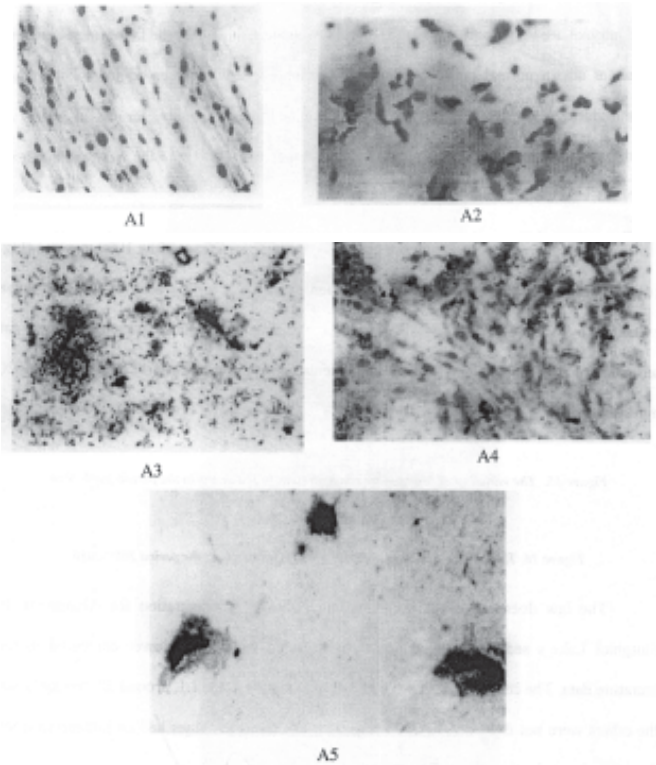

Fig. 6. Images taken by optical microscopy on studied samples. A1 blank culture, human foetus fibroblast.; A2- medical PVC, A3-inner surface of the hollow body with antimicrobial agent based on $AgCl/TiO_2$;A4-inner surface of the hollow body AgCl / silica as antimicrobial agent; A5-cytotoxic positive control on the basis of PVC stabilized with an organometallic compound.

The analysis of the images shown in figure 6 highlights the antimicrobial properties of ionic silver incorporated into the inner layer of hollow bodies.

Antimicrobial agents based on high $AgCl/TiO_2$ are due to a synergistic effect of the titanium dioxide itself, acting in this respect.

Conclusions

Studies carried out in order to obtain the antimicrobial hollow bodies have led to the following conclusions:

- the physico-mechanical properties are superior to polypropylene without additives, which suggests a reinforcing effect of silver chloride deposited on TiO_2 or silica;
- the compositions used in the process lead to more transparent hollow bodies than those obtained from native polypropylene;
- due to their superior properties, the products can substitute similar packages of glass, PET and PC, which are more expensive and energy consumming;
- biocompatibility tests revealed that the obtained materials exhibit antimicrobial properties, which recommend them for the use in production of products and devices for medical or cosmetic and food packaging.

Composites based on $AgCl/TiO_2$ show antimicrobial properties superior to those based on AgCl/silica, which suggests a synergistic effect, as titanium dioxide is itself an antimicrobial agent.

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