

## POLY(VINYL ALCOHOL)/POLY(LACTIC ACID) BLENDS BIODEGRADABLE FILMS DOPED WITH COLLOIDAL SILVER

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Received September 20, 2007

The study describes the preparation and characterization of some biodegradable films obtained from PVA/PLA blends (100/0, 90/10, 80/20, 70/30), colloidal Ag<sup>0</sup> and other additives. Poly(lactic acid) was synthesized by melt polycondensation procedure of L(+)-lactic acid using manganese acetate as catalyst. The films were carried out by solution casting and evaporation of the solvents water/dioxane at ambient temperature. The films were characterized by IR spectroscopy, mechanical properties, thermal analyses (DSC, DTG) and optical microscopy.

### INTRODUCTION

Research on biodegradable materials has been stimulated and developed to overcome problems regarding the persistence of plastic wastes in the environment. Biodegradable materials are used and studied in an increasingly number of applications (packaging, paper coating and other disposable articles), as well as in biomedical applications (resorbable surgical sutures, implants and controlled drug delivery devices). Polyesters such as poly(lactic acid), poly(caprolactone) (PCL) and poly(glycolic acid) (PGA) are biodegradable and biocompatible polymers. They can be degraded into small molecules through hydrolytic or enzymatic degradation.

Poly(vinyl alcohol) is a great interest biodegradable, biocompatible and non-toxic polymer with various applications such as: fibres, protection colloids, sizing agents for textiles and paper, adhesives, moulded sheets, suture fibres in surgery, membranes. These properties come jointly with a remarkable chemical versatility due to the presence of the hydroxylic groups, which make feasible a number of grafting and crosslinking reactions of the polymer backbone. The modification of secondary hydroxyl groups of PVA has been reported in the literature to obtain materials with new properties.<sup>1-3</sup> PVA derivatives soluble in cold water with a lower T<sub>g</sub> and good

mechanical properties have been synthesized by reacting hydroxyl groups with lactic and glycolic acids.<sup>4-6</sup> Also, PVA blends with other polymers: polyolefins, poly(acrylic acid), poly(sodium aspartate), poly(methyl methacrylate), poly(acrylamide) were reported, thus leading to new materials with superior properties.<sup>7</sup>

Poly(lactic acid), a thermoplastic polyester, is also suitable for packaging applications, since its glass transition temperature (about 60 °C) is above the service temperature and therefore a good barrier material for solvents, flavors, aromas and a medium barrier for permanent gases.<sup>8</sup> Poly(lactic acid) has been attracting much attention because it has excellent mechanical properties, is hydrolyzable and non-toxic in diverse environments as well as in the human body.<sup>9-13</sup> Tensile strength and modulus of elasticity of PLA are comparable to poly(ethylene terephthalate) (PET). The enzymatic hydrolysis rate of polylactides decrease with a rise in their crystallinity.<sup>14-17</sup> This is due to higher enzymatic hydrolysis rate of PLA chains in the amorphous region than in the crystalline ones.

Silver-based antibacterial materials attracted much attention because of their long-term biocidal activity, nontoxicity as well as perfect antibacterial activity.<sup>18-20</sup> Silver is a powerful, natural prophylactic antibiotic used for thousands of years on external wounds and burns to prevent infection. One of the primary motives for the development of silver

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containing materials is due to the adhesion of bacteria onto various surfaces which leads to the formation of infectious biofilms. Biofilms are formed when bacterial cells adhere to a solid, wet surface and begin to aggregate, forming organized microcolonies.<sup>21</sup> Silver has long been recognized as having an inhibitory effect toward many bacterial strains and microorganisms present in industrial and medical processes<sup>22</sup> in its oxidation states:  $\text{Ag}^0$ ,  $\text{Ag}^+$ ,  $\text{Ag}^{2+}$ ,  $\text{Ag}^{3+}$ . The most widely utilized applications of silver and silver nanoparticles are in the medical industry (antibacterial wound dressings and bandages, catheters and implantable hip and joint replacements that inhibit post-surgical bacterial infections). Dispersions of minuscule silver particles in water, also known as colloidal silver, have commonly been used as disinfectants. The exact mechanism by which silver inhibits microbial growth is not entirely understood. It is believed that heavy metals release ions which react with the thiol groups of surface proteins. Monovalent silver ions ( $\text{Ag}^+$ ) are believed to replace the hydrogen cation ( $\text{H}^+$ ) of thiol groups, inactivating the protein, decreasing membrane permeability and eventually causing cellular death.<sup>23</sup>

In addition to the medical industry, silver embedded fabrics are used in sporting equipment, children's toys and silver impregnated polymers as antimicrobial food packaging materials. Silver nanoparticle-coated polyethylene polymer sheets which release silver ions and silver nanoparticles and fabric sheets made of silver-coated polyamide fibers were obtained.<sup>24</sup> Microbial growth prevention has become increasingly important also in the textile industry, because common natural and synthetic fibers used for textile fabrication lack antimicrobial properties. Organic compounds such as halogenated aromatics were employed in textile finishing processes as antibacterial agents,<sup>25</sup> but these compounds are highly toxic environmental pollutants. Polypropylene (PP), one of the most widely used synthetic materials in the textile industry has no antimicrobial properties. An organic-inorganic nanocomposite fiber displaying permanent antibacterial activity by combining PP chips and silver nanoparticle containing PP master batches via conventional twin-screw extrusion was designed. Also, electrospinning was employed for fabrication of PVA/Ag nanofibers with bactericidal properties for bandages and wound dressings.<sup>26</sup>

In the present paper we report some preliminary results regarding the mechanical and thermal

properties of films based on PVA/PLA blends with  $\text{Ag}^0$  nanoparticles and other additives.

## EXPERIMENTAL

### Materials

Poly(vinyl alcohol) (PVA 40-98) from S.C. Romacryl-SA Raşnov (Roumania) with hydrolysis degree 98 % and polymerization degree 400, average molecular weight  $M_n=18000$ , saponification index  $140 \pm 30$  mg KOH/g was used. Poly(lactic acid) was synthesized in the laboratory from L(+)-lactic acid (Fluka, Switzerland) using a melt polycondensation procedure. Sodium tetraborate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , glycerol, dioxane were analytical grade reagents (Fluka, Switzerland), and were used as received. Colloidal silver (nanoparticles size 40 nm) was prepared by catalytic reduction of silver nitrate ( $\text{AgNO}_3$ ) with sodium citrate ( $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 5\text{H}_2\text{O}$ ).

### Characterization

FTIR spectra were recorded using a Digilab Scimitar Series (USA) spectrophotometer with  $4 \text{ cm}^{-1}$  resolution. The samples were homogenized and pressed on KBr pellets.

Thermogravimetric analyses (TG and DTG) were carried out using a derivatograph Q-1500 D (MOM Budapest, Hungary) at the following conditions: the weight of the sample 50 mg, the heating rate  $10 \text{ }^\circ\text{C}/\text{min}$ , the maximum heating limit  $700 \text{ }^\circ\text{C}$ , reference material  $\alpha\text{-Al}_2\text{O}_3$ .

Thermal DSC analyses were carried out by means of a Mettler 12E type differential scanning calorimeter (Switzerland) with a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$  in nitrogen atmosphere. The first heating run was carried out with a 10-12 mg sample in the temperature range between room temperature and  $300 \text{ }^\circ\text{C}$ . The second heating run was performed with samples which were suddenly cooled to room temperature. Pure indium was used as a standard for calorimetric calibration.

The mechanical measurements of the films were recorded with a TIRA-TEST-2200 (Germany) type tensile test apparatus at a drawing speed of 30 mm/min. Test samples with surface areas of  $60 \times 6$  mm and 100-200  $\mu\text{m}$  thickness were used. The active length of the sample was 30 mm. Before submitting the samples to the tensile test, they were maintained 3h in a vacuum oven at  $50 \text{ }^\circ\text{C}$  and residual pressure of 0.01daN. For all samples 5 determinations were carried out and the result was given as an average.

Optical microscopy studies were done using a microscope MICROS-MCD 500 (Austria) with incorporated video chamber and PC software.

### Procedure

To carry out films by solution casting procedure, PVA and PVA/PLA mixtures with gravimetric ratio 100/0, 90/10, 80/20, 70/30 were used. Sodium tetraborate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  was included in the film composition as crosslinking agent, glycerol as plasticizer and colloidal silver as antimicrobial agent. Poly(lactic acid) was synthesized by melt polycondensation procedure of L(+)-lactic acid using manganese acetate as catalyst.<sup>27</sup> In poly(vinyl alcohol) aqueous solution (9.85 wt.%), glycerol 10 wt.% reported to PVA was added. The mixture was maintained under stirring at

25°C, then PLA solution in dioxane (19.4 wt.%) was added. The mixture was heated at 70 °C for 30 minutes, vacuum filtered by a gooch crucible, then colloidal silver solution (50 ppm reported to polymer mixture) was added. The mixture was maintained under stirring for 15 minutes, then sodium tetraborate (5 wt.% aqueous solution) was added. The crosslinking agent was used 0.5 wt.% and 1 wt.% reported to

the two polymers in the blend. The final solution obtained was used to carry out films by casting on a glass plate, followed by drying at 25-30°C for 72h and films with thickness 100-200 µm were obtained. The composition of films carried out from PVA and PVA/PLA mixtures with or without colloidal silver and crosslinked with sodium tetraborate is presented in Table 1.

Table 1

Film composition obtained from PVA and PVA/PLA mixture with colloidal silver nanoparticles.

Sample	PVA/PLA (g)	PVA aqueous solution 9.85 wt.% (g)	PLA dioxane solution 19.4 wt.% (g)	Glycerol (mL)	Ag <sup>0</sup> colloidal solution 10 <sup>-3</sup> M (mL)	Borax aqueous solution 5 wt.% (mL)
1	100/0	20.30	-	0.16	0.92	-
2	100/0	20.30	-	0.16	0.92	0.20
3	100/0	20.30	-	0.16	0.92	0.40
4	100/0	20.30	-	0.16	-	0.40
5	90/10	18.30	1.04	0.14	0.92	-
6	90/10	18.30	1.04	0.14	0.92	0.18
7	90/10	18.30	1.04	0.14	0.92	0.36
8	90/10	18.30	1.04	0.14	-	0.36
9	80/20	24.36	3.09	0.20	1.38	-
10	80/20	24.36	3.09	0.20	1.38	0.24
11	80/20	24.36	3.09	0.20	1.38	0.48
12	80/20	24.36	3.09	0.20	-	0.48
13	70/30	21.30	4.64	0.18	1.38	-
14	70/30	21.30	4.64	0.18	1.38	0.21
15	70/30	21.30	4.64	0.18	1.38	0.42
16	70/30	21.30	4.64	0.18	-	0.42

## RESULTS AND DISCUSSION

FTIR spectra of PVA-Ag<sup>0</sup> and PVA/PLA-Ag<sup>0</sup> films with 1 % crosslinking agent are presented in figure 1. In IR spectrum of the films carried out from PVA/PLA-Ag<sup>0</sup> mixture most of the absorption bands characteristic to PVA: 3424 cm<sup>-1</sup> (νOH); 2927 cm<sup>-1</sup> (νCH<sub>2</sub>); 2844 cm<sup>-1</sup> (νCH); 1450 cm<sup>-1</sup> (δCH<sub>2</sub>) and 1100 cm<sup>-1</sup> (νC=O) characteristic to residual unhydrolyzed acetyl groups are found. Besides, the presence of an absorption band at 1730 cm<sup>-1</sup> (νC=O) corresponding to COOR ester group and at 1590-1600 cm<sup>-1</sup> (νC=O) corresponding to COO<sup>-</sup> anion ester group, was noticed. Also, the presence of a shoulder between 1310-1380 cm<sup>-1</sup> characteristic to (νB-O) group was recorded as a result of PVA crosslinking with sodium tetraborate.

The tensile strength, elongation at break and tensile modulus were determined at room temperature to ascertain the films quality in a packaging use for instance.

The tensile strength of the films is presented in Fig. 2. In the case of films achieved only from

PVA, the crosslinking agent (sodium tetraborate) determines the tensile strength increase: 12.28-14.06 N/mm<sup>2</sup> comparative to 11.40 N/mm<sup>2</sup> in the case of uncrosslinked films. The presence of colloidal silver nanoparticles in films composition does not modify significantly the tensile strength value. In the case of films obtained from PVA/PLA blends the tensile strength value is lower comparative to PVA sample excepting sample 7, the values are not constant and vary between 3.44-15.16 N/mm<sup>2</sup>. Also, it was noticed that films obtained from crosslinked PVA/PLA blends and Ag<sup>0</sup> nanoparticles have higher tensile strength than uncrosslinked films with Ag<sup>0</sup> or crosslinked but without Ag<sup>0</sup> in the composition. This fact indicates the synergism effect of the crosslinking agent and of Ag<sup>0</sup> nanoparticles on the films. We can notice (Fig. 2) that almost constant values of the tensile strength were obtained only in the case of PVA/PLA (80/20) ratio. At PVA/PLA 70/30 ratio the influence of the crosslinking agent is lower because PVA content decreases in the mixture and borax is a specific crosslinking agent for this polymer.

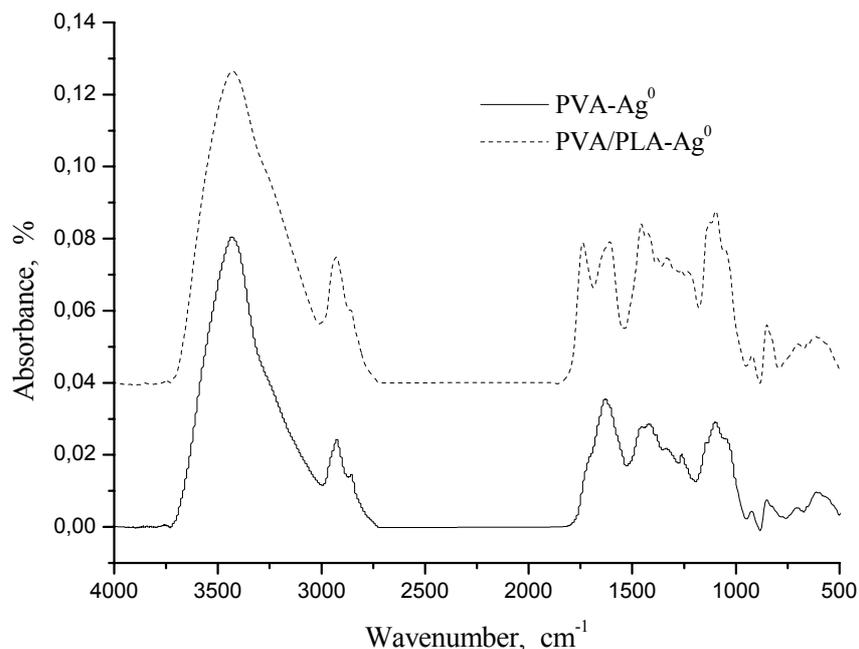


Fig. 1 – FTIR spectra of PVA-Ag<sup>0</sup> and PVA/PLA-Ag<sup>0</sup> films with 1 % crosslinking agent.

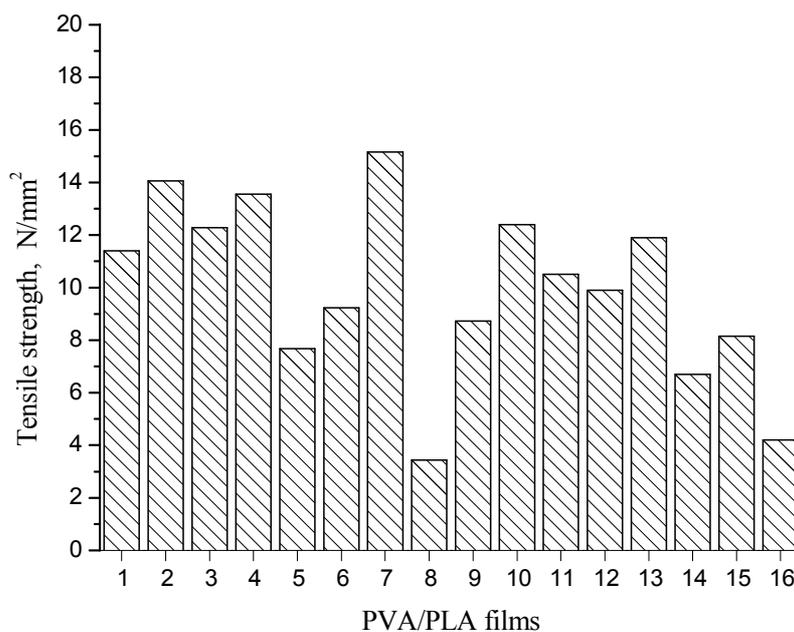


Fig. 2 – Tensile strength of films obtained from PVA and PVA/PLA mixture.

The elongation at break of PVA and PVA/PLA films is presented in Fig. 3. In the case of PVA films the elongation at break varies between 236.1-385.6% and in the case of PVA/PLA ones between 109.2-347.9%. In all cases it was ascertained that uncrosslinked films with Ag<sup>0</sup> nanoparticles or with 0.5 wt.% crosslinking agent presented higher values of the elongation at break. The increase of crosslinking agent concentration at 1 wt.% determines a visible lowering of the elongation at break unaffected by the presence or the absence of

Ag<sup>0</sup> nanoparticles in the composition. The higher values of the crosslinking agent determine macromolecular chains mobility lowering and implicitly the elongation at break. The modification of PVA/PLA ratio does not influence significantly the elongation at break.

Another parameter evaluated for PVA and PVA/PLA films is the elasticity modulus (Fig. 4). Its value is comprised between 55.25-266.80 N/mm<sup>2</sup> for PVA films and between 89.15-391.00 N/mm<sup>2</sup> for PVA/PLA films. Also, in this case we

notice the synergetic effect of the crosslinking agent and of  $\text{Ag}^0$  nanoparticles on the elasticity modulus. In some cases (3, 7, 11 and 15 samples) the elasticity modulus value is twice higher than of

films achieved from the same PVA/PLA ratio, but only with  $\text{Ag}^0$  or crosslinking agent added in the composites.

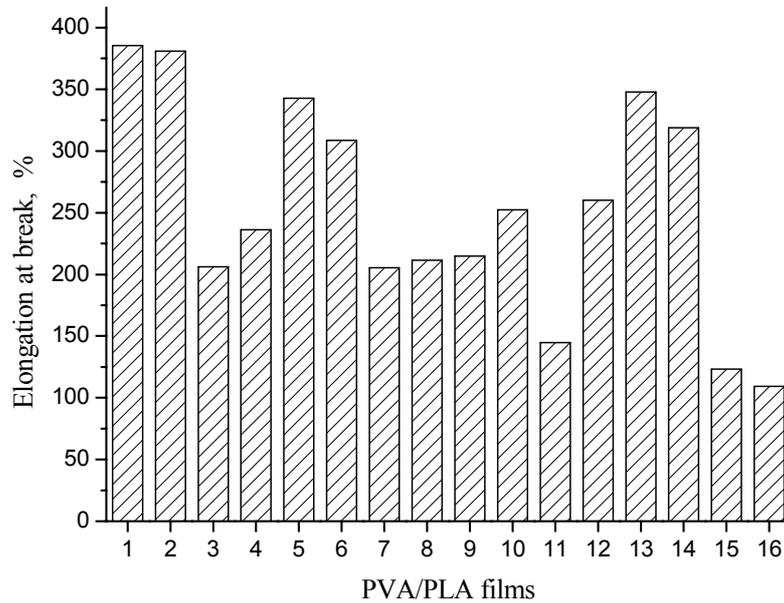


Fig. 3 – Elongation at break of PVA and PVA/PLA films.

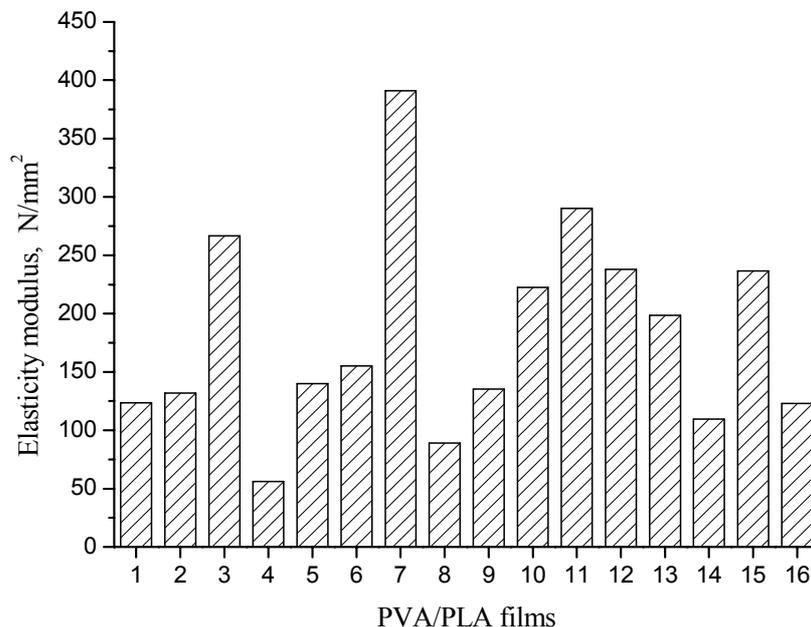


Fig. 4 – Elasticity modulus of PVA and PVA/PLA films.

The weight losses recorded by oxidative thermal decomposition (TG) of some samples are presented in Figs. 5 and 6 and some data concerning the thermal stability and the kinetic parameters ( $E_a$ ,  $n$ ) in Table 2. The thermogravimetric curves present three main thermal decomposition processes which take place

with different rates. The films carried out from PVA/PLA- $\text{Ag}^0$  blends present a higher thermal stability comparative to films from PVA/ $\text{Ag}^0$  (Table 2). For example, in the case of PVA- $\text{Ag}^0$  films weight losses of 50 % ( $T_{50}$ ) are recorded at 285°C, while in the case of PVA/PLA- $\text{Ag}^0$  these losses are recorded at 365-385°C. Also, we notice

that in the case of PVA/PLA-Ag<sup>0</sup> films crosslinked with sodium tetraborate 1 wt.% (samples 11 and 15) the thermal stability is higher than of uncrosslinked films (samples 9 and 13). The activation energy (E<sub>a</sub>) and reaction order (n) were determined in each case on the main decomposition process T<sub>i</sub>-T<sub>f</sub> (150-380<sup>o</sup>C) using the

literature given methods.<sup>28, 29</sup> These parameters are higher in the case of PVA/Ag<sup>0</sup> films, comparative to PVA/PLA-Ag<sup>0</sup> films. The weight losses determined on T<sub>i</sub>-T<sub>f</sub> interval have values 39-45 wt.% in the case of films prepared from PVA/PLA-Ag<sup>0</sup> mixture and 61.6 wt.% in the case of films prepared from PVA/Ag<sup>0</sup>.

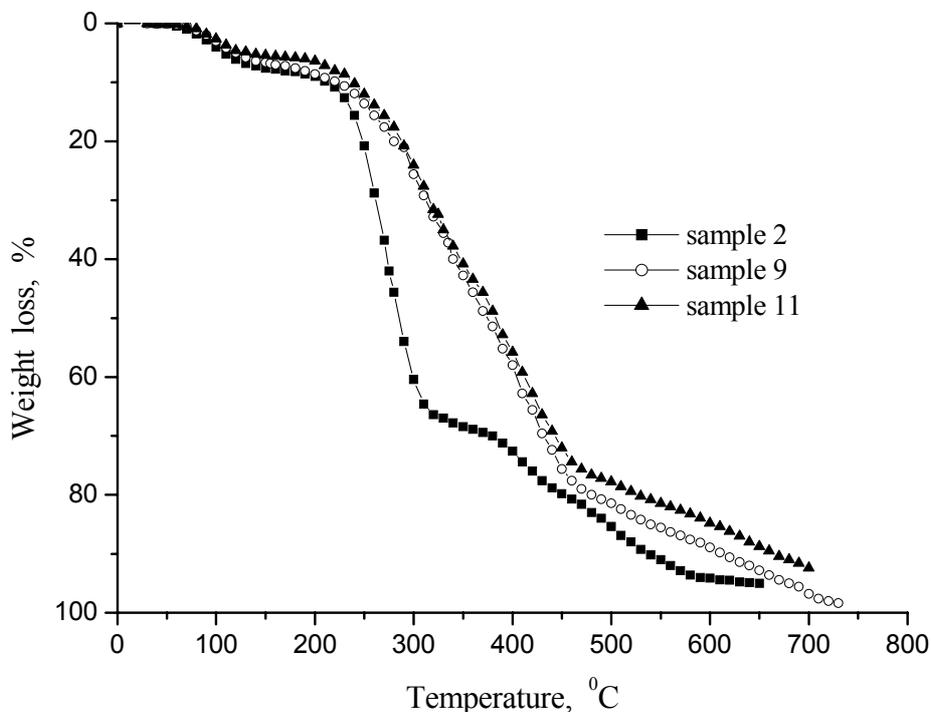


Fig. 5 – Weight losses by oxidative thermal decomposition.

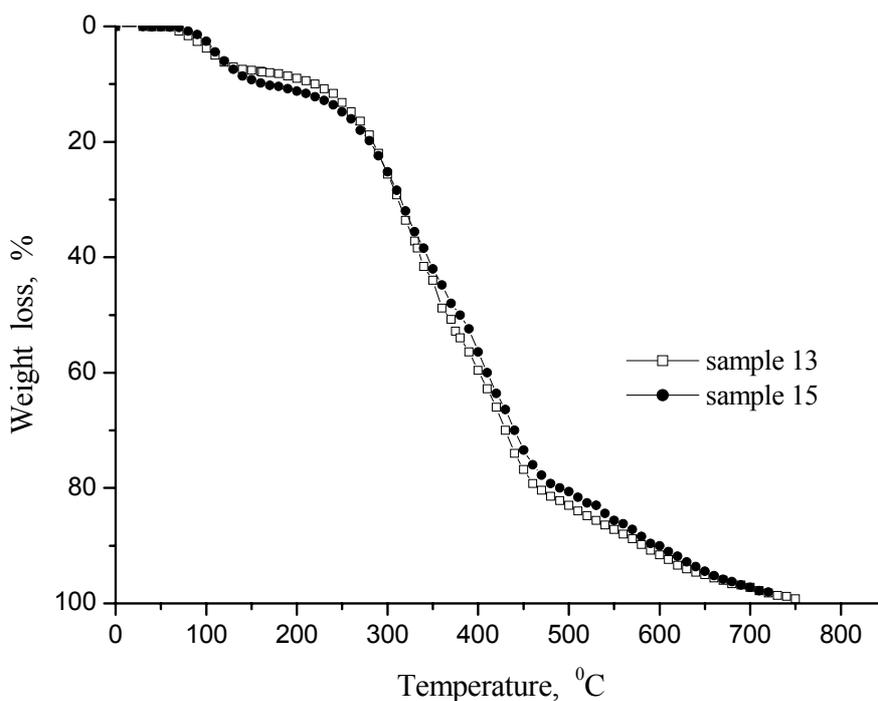


Fig. 6 – Weight losses by oxidative thermal decomposition.

Table 2

Parameters determined by DTG analyses.

Sample	T <sub>10</sub> (°C)	T <sub>50</sub> (°C)	T <sub>i</sub> (°C)	T <sub>m</sub> (°C)	T <sub>f</sub> (°C)	W <sub>T<sub>i</sub>-T<sub>f</sub></sub> (%)	Ea (kJ/mol)	n
2	165	285	160	275	370	62	94.68	1.5
9	210	378	155	335	370	42	56.68	1.0
11	230	385	150	325	365	39	64.54	1.0
13	210	365	162	333	375	45	70.69	1.2
15	185	380	180	340	380	40	62.22	0.9

T<sub>10</sub>, T<sub>50</sub> - temperature corresponding to 10 % and 50 % weight loss.T<sub>i</sub>, T<sub>f</sub> - the initial and ultimate temperature of the domain on which Ea and n were calculated.T<sub>m</sub> - temperature corresponding to weight losses taking place at maximum speed.

W - weight losses.

Ea, n - activation energy and reaction order.

DSC analyses are presented in Fig. 7 and Table 3. The melting temperature (T<sub>m</sub>) of PVA films is situated between 210-212 °C, the glass transition temperature (T<sub>g</sub>) value between 55-57 °C. The values are lower than of corresponding PVA (T<sub>m</sub> = 228 – 240 °C; T<sub>g</sub> = 70 – 80 °C), due to film plasticization with glycerol.<sup>30</sup> In most of the DSC curves an exothermic process is noticed at 140-145 °C due to the presence of glycerol in the composition, which has burning point at 160 °C.

T<sub>m</sub> and T<sub>g</sub> values are slightly higher in the case of films doped with colloidal silver nanoparticles (sample 4). In the case of films obtained from PVA/PLA mixture, the melting temperatures are lower (202-206 °C), and T<sub>g</sub> values are comprised between 50-68 °C and vary with film composition. The melting enthalpy has values ranging between 57.96-97.85 J/g and varies with PVA/PLA ratio, the presence of colloidal Ag<sup>0</sup> and the concentration of the crosslinking agent.

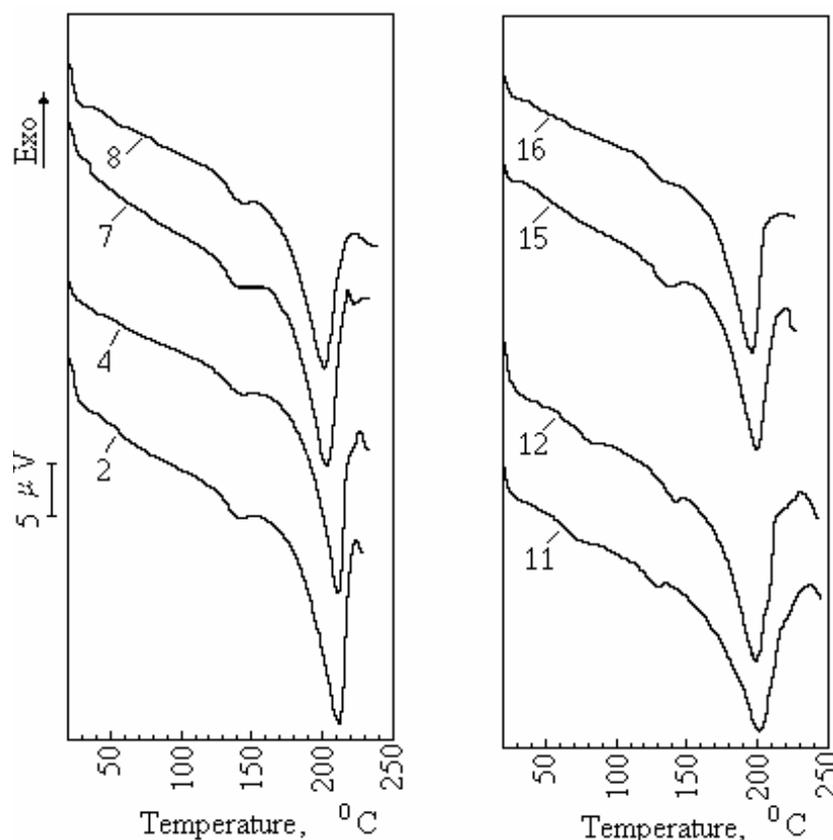


Fig. 7 – DSC diagrams of PVA films and PVA/PLA mixtures with colloidal silver.

Table 3

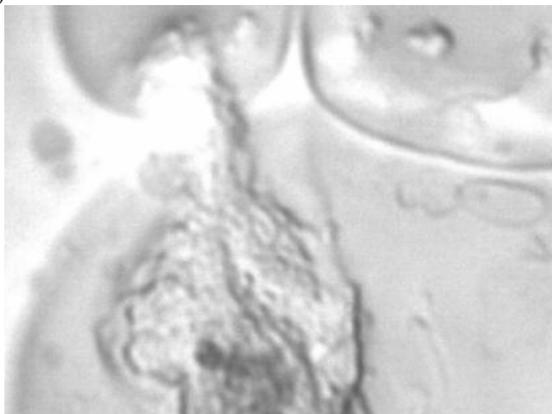
Parameters determined by DSC analyses

Sample	Tg (°C)	Tm (°C)	ΔH (J/g)
2	55	210	64.18
4	57	212	58.76
5	63	205	66.44
7	55	204	69.05
8	59	202	62.90
9	60	205	68.37
11	57	202	97.85
12	58	202	92.50
13	55	206	76.33
15	68	202	62.90
16	50	202	57.96

The morphology of the films surface cast from PVA/PLA solutions was studied by optical microscopy. In figure 8a the optical microscopy of PVA/PLA (80/20) film crosslinked with 1 wt.% sodium tetraborate without colloidal Ag<sup>0</sup> nanoparticles is presented. The presence of two phases belonging to the polymers, as well as the presence of the plasticizer (glycerol) as oil in water droplets can also be noticed in the films. The photography presented in Fig. 8b belongs to a

PVA/PLA (90/10) film with colloidal Ag<sup>0</sup> nanoparticles and crosslinked with 1 wt.% sodium tetraborate. In this case, we can also see the presence of phases belonging to polymers, glycerol, and silver nanoparticles. Colloidal Ag<sup>0</sup> nanoparticles are transformed in solution in Ag<sup>+</sup> ions which are physically associated and adsorbed at the surface of the phases, preponderant at the surface of polylactic acid phase that present carboxylic groups.

a)



b)

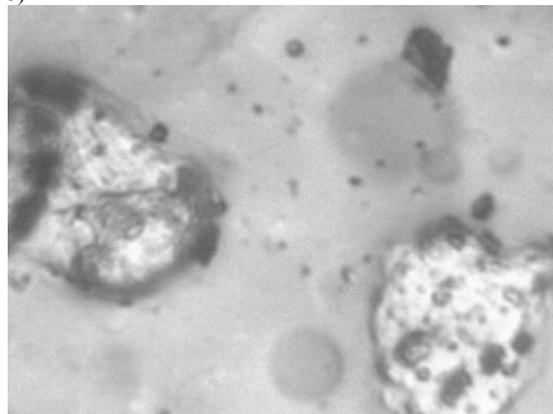


Fig. 8 – Optical microscopy: a) PVA/PLA film (80/20) with 1 wt.% sodium tetraborate (magnitude 100<sup>\*</sup>); b) PVA/PLA film -Ag<sup>0</sup> (90/10) with 1 wt.% sodium tetraborate (magnitude 100<sup>\*</sup>).

## CONCLUSIONS

Biodegradable films from PVA and PVA/PLA blends doped with colloidal silver nanoparticles with possible utilization in packaging have been obtained.

The films carried out from PVA/PLA-Ag<sup>0</sup> blends present lower mechanical properties comparative to PVA/Ag<sup>0</sup> films. The light lowering of the mechanical properties indicate that PVA/PLA blends are partially compatible. Generally, the tensile strength of crosslinked films

with or without Ag<sup>0</sup> nanoparticles increases, comparative with uncrosslinked films due to intermolecular links established between PVA macromolecules in the composite. The elongation at break and tensile modulus decrease with crosslinking agent increase, thus determining the chains mobility lowering.

Films achieved from PVA/PLA blends with Ag<sup>0</sup> nanoparticles and crosslinked with sodium tetraborate have higher thermal stability comparative to PVA/Ag<sup>0</sup> films, suggesting their possible use in packaging.

Ag<sup>0</sup> nanoparticles present a bactericide character, and PLA - a hydrophobic polymer determines the growth humidity resistance of the obtained films with possible utilization in medical or pharmaceutical field.

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