

Poly(vinyl alcohol)-*g*-Lactic Acid Copolymers and Films with Silver Nanoparticles

Nita Tudorachi, Rodica Lipsa

"Petru Poni" Institute of Macromolecular Chemistry, Polymer Materials Department, Iasi, 700487, Romania

Received 26 February 2010; accepted 26 January 2011

DOI 10.1002/app.34241

Published online 20 May 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Poly(vinyl alcohol) (PVA), a well-known synthetic biodegradable, biocompatible, and hydrophilic polymer is susceptible to several structural modifications, due to the presence of hydroxyl groups in its backbone. PVA was grafted with L(+)-lactic acid (LA) in molar ratios VA/LA (1/1, 1.5/1, and 2.2/1), manganese acetate as catalyst, by solution polycondensation procedure, resulting the poly(vinyl alcohol)-*g*-lactic acid copolymers. Aqueous solutions of copolymers with glycerol as plasticizer, silver nanoparticles (Ag⁰), and sodium tetraborate as crosslink-

ing agent were used for films casting. The copolymers were characterized by FTIR and ¹H RMN spectroscopy, gel permeation chromatography, thermal analyses (DTG and DSC), silver particles size, while films were characterized by mechanical properties and mechanodynamic analyses. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1109–1120, 2011

Key words: copolymers; silver nanoparticles; L(+)-lactic acid; poly(vinyl alcohol); films

INTRODUCTION

Modification of conventional polymers is an important technique in the synthesis of new materials with improved properties. Poly(vinyl alcohol) (PVA) is a polymer with excellent properties: hydrosoluble, biocompatible, biodegradable, nontoxic, noncarcinogenic, consequently films with high mechanical strength and reduced permeability to gases can be prepared. PVA with a raised structural variability (molecular weight, hydrolysis degree, and tacticity), due to the presence of hydroxyl moiety in its backbone is capable of several grafting and crosslinking reactions with acid chlorides, acid anhydrides, acrylamide, lactic acid (LA) and LA oligomers, glycolic acid.^{1–4} The obtained copolymers that contain different numbers of carboxyl groups are of great interest in the paper industry, as modifiers of thermosetting resins in plywood manufacture, and as pressure sensitive adhesives.⁵ In addition, PVA polymers that contain carboxyl groups can react in a further step with difunctional compounds, leading to three-dimensional networks. Besides, biodegradable aliphatic polyesters such as: polylactide (PLA), poly(*ε*-caprolactone), copolymers of lactides and glycolide (PLGA), poly(β -hydroxybutyrate) (PHB), and poly(*p*-dioxanone) (PPDO) have attracted much attention

in recent years, because of their excellent biocompatibility and biodegradability and have been widely utilized in biomedical and pharmaceutical applications, such as surgery repair materials and drug-delivery systems.^{6–9} The biodegradable polyesters are highly hydrophobic and therefore have caused some limitations in practical drug formulations. Many synthetic methods were developed to synthesize various kinds of copolymers with different structures and compositions. One useful strategy to modify the physicochemical and biological properties of hydrophobic polyesters is the incorporation of hydrophilic poly(ethylene glycol) (PEG) and PVA segments. The biodegradation rate and hydrophilicity of block copolymers can be modulated by adjusting the ratio of its hydrophilic and hydrophobic constituents. The introduction of an aliphatic polyester on PVA backbone, by graft copolymerization would induce the control of degradability and physical properties, by modifying the chemical structure of the graft copolymer (when the polymerization conditions are changed).

Concerning the importance of colloidal silver to human body, numerous researches were carried out to achieve particles of nanometric size, and subsequently they were encapsulated or complexed in polymer matrices. The composite materials, acquired by inclusion of metallic or ionic silver in polymer matrices focused the researchers attention, because of their potential applications in important fields as medicine (catheters and materials with biocompatible and antimicrobial properties, dedicated to implants),^{10,11} nanoelectronics (optical and interference filters),^{12,13}

Correspondence to: N. Tudorachi (tudorachinita@yahoo.com).

filtering stations of drinkable water in countries with reduced water potential.¹⁴ Silver nanoparticles refer to particles with $<1\ \mu\text{m}$ dimensions that are in the oxidation state Ag^0 and optionally Ag^{1+} and Ag^{2+} . Silver is a strong natural antioxidant that can react with free radicals in the organism. In either oxidation states, silver and its compounds are largely utilized as antimicrobial agents,^{15,16} the most important one is silver sulfadiazine (as it has a large spectrum of antibacterial activity), although there exist other compounds with antimicrobial properties (silver acetate, silver nitrate, metal silver, etc). Other applications of silver nanoparticles are in the field of medical devices and implants, achieved with polymers impregnated with silver. The contact lenses can be exposed during utilization, storage, or handling to one or more species of microorganisms. On the surface of contact lenses can adhere microorganisms that proliferate colonies generation for long periods of time and cause infection or disease of the eyes. There were achieved contact lenses with resistance to microorganisms,¹⁷ using silver nanoparticles with antimicrobial activity. The method consisted in preparing a fluid polymerizable composition, with a siloxane macromer and a vinyl monomer capable of reducing Ag^+ cations from AgNO_3 or AgClO_4 .

The article presents the modification reaction of PVA with $\text{l}(+)\text{-LA}$, in the presence of $(\text{CH}_3\text{COO})_2\text{Mn}\cdot 4\text{H}_2\text{O}$ as catalyst. The syntheses were done by solution polycondensation procedure, using the following VA/LA molar ratios: 1/1, 1.5/1, and 2.2/1. The reactives used in copolymers synthesis were biodegradable and biocompatible compounds. PVA polymer and poly(vinyl alcohol)-*g*-lactic acid (PVA-*g*-LA) copolymers were utilized to prepare films by casting from aqueous solution, in the presence of a crosslinking agent (sodium tetraborate), plastifying agent (glycerol), and silver colloidal nanoparticles. Films with 150- to 250- μm thickness were achieved, and the concentration of silver nanoparticles reported to PVA or PVA-*g*-LA gravimetric weight, respectively, was 40 ppm. Silver nanoparticles incorporation and PVA-*g*-LA solubility in different organic solvents represent an important advantage as the products, due to their bacteriostatic character can be utilized as polymer covering layers or in medical and pharmaceutical packaging.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA 40-98) from SC Romacryl SA (Romania) had a degree of hydrolysis 98%, average molecular weight $M_n = 18,000$, saponification index $140 \pm 30\ \text{mg KOH/g}$. $\text{l}(+)\text{-LA}$ 90 wt % aqueous solution, density 1.20 g/mL was supplied

by Fluka (Switzerland). Manganese acetate [$\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$], methylene chloride, *N,N*-dimethylformamide (DMF), glycerol, sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$) analytical reagents (Fluka) and acetone from Chimopar S.A. (Romania) were used, without further purification. Silver nanoparticles were obtained by catalytic reduction of silver nitrate (AgNO_3) with sodium citrate ($\text{C}_6\text{H}_5\text{O}_7\text{Na}_3\cdot 5\text{H}_2\text{O}$).

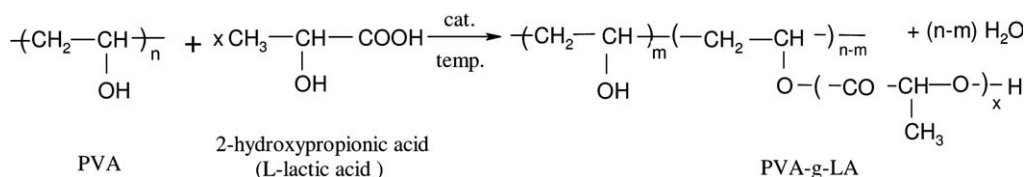
Copolymer synthesis

In PVA-*g*-LA copolymers syntheses, PVA and LA aqueous solutions were used. The copolymers were synthesized in the presence of manganese acetate as catalyst and at appropriate reaction temperatures. The reaction mechanism is presented in Scheme 1. The copolymers synthesis was done using three VA/LA molar ratios and $\text{C}_1\text{-C}_3$ copolymers (see Table I) were obtained. It was achieved in a glass reaction vessel, equipped with mechanical stirrer, thermometer, blanket of nitrogen, Dean-Stark distillation trap (for secondary reaction products collection), and heating bath with silicon oil. PVA was dissolved in distilled water, under stirring at 70–80°C, then corresponding quantities of LA and manganese acetate catalyst (0.8 wt % reported to components) were added. The reaction mass was kept under blanket of nitrogen and reflux at 96–98°C for 3 h, then the temperature was raised at 120–130°C and water, as solvent and secondary reaction product was removed. Furthermore, the collection of secondary reaction products was discontinuous and the reaction mass was maintained under reflux for another 3 h to be finalized. The resulted product was precipitated in a large volume of acetone, filtrated, and vacuum dried at 70°C. Then, the product was again dispersed in a large volume of methylene chloride and was maintained under stirring for 2 h at 20°C to remove PLA homopolymer also resulted in the synthesis. The copolymer was finally separated by centrifugation and dried in a vacuum oven at 50°C until the solvent was completely removed.

The PVA-*g*-LA copolymers reaction yields were 68–76 wt % and depended on the components molar ratio utilized in the syntheses. By PVA grafting with LA, its hydrophobic character increased.

Films preparation

To achieve films, aqueous solutions of PVA, PVA-*g*-LA copolymers ($\text{C}_1\text{-C}_3$), glycerol, sodium tetraborate, and silver nanoparticles were used in appropriate ratios. The components ratio is presented in Table I. Colloidal silver solutions were performed according to Lee and Meisel.¹⁸ Approximately 90 mg of AgNO_3 was dissolved in 500 mg of bidistilled water and heated to boiling, while being vigorously



Scheme 1 Synthesis mechanism of PVA-g-LA copolymer.

stirred. The reduction of silver salt was accomplished by adding 10 mL sodium citrate aqueous solution 1 wt %. The solution was maintained at boiling for about 1 h, in the end the color of the colloidal solution was greenish-yellow. The UV spectra of bulk silver colloids, recorded with a spectrophotometer 6305-UV/VIS model presented a large absorption band and revealed extinction maxima at ~ 420 nm (Fig. 1). These results agree with the spectra of Ag colloidal solutions, given in the literature.^{18,19}

The nanoparticles size is about 350 nm, as measured by laser light diffusion method (Fig. 2) and scanning electron microscopy (SEM) (Fig. 3). The presence of spherical Ag nanoparticles and agglomerated particles can be seen. This notice indicates that a low degree of agglomeration of Ag particles can occur during their incorporation into the polymer matrix. Despite the observed agglomeration, the films maintain their optical clarity. The concentration of silver nanoparticles reported to PVA or PVA-g-LA copolymers gravimetric weight was 40 ppm. By modifying PVA with LA, its hydrophobic character and consequently films humidity resistance slightly increased. Glycerol, as plastifying agent (10 wt %), and sodium tetraborate (crosslinking agent), as aqueous solution, 0.5 wt % reported to PVA or PVA-g-LA copolymers were utilized. The films were carried out by solution casting and solvent removal was done by air drying.

Characterization

IR spectra were recorded using a spectrophotometer M 80 Specord model (Germany). The samples were

homogenized and pressed on KBr pellets (5-mg sample/500-mg KBr).

¹H NMR spectra were recorded with a Bruker Avance DRX 400 NMR spectrophotometer model (Germany). The copolymers were dissolved in D₂O and the sample concentration was about 5 wt %. The spectra were carried out at 25°C, all chemical shifts were reported in parts per million (ppm), and tetramethylsilane was used as the internal reference.

Thermogravimetric analyses (TGs) were carried out using a Paulik–Paulik–Erdley-type derivatograph (MOM Budapest, Hungary) under the following operational conditions: the weight of the sample, 50 mg; heating rate, 10°C/min; maximum heating limit, 700°C; reference material, α -Al₂O₃ in air stream.

Measurement of particle size was performed in aqueous solutions (1 g/dL) with a Zetasizer Nano-ZS instrument, ZEN-3500 model (Malvern Instruments, UK) by laser light diffusion method. For measurements, the silver nanoparticles were dispersed in bidistilled water at a concentration of 1g/L and ultrasonicated for 60 s. The measurement was carried out using a laser green light He-Ne (532 nm) as light source at a fixed angle of 173°. The following parameters were used for experiments: water as dispersant medium with a refractive index 1.330, viscosity 0.887 cP, and temperature 25°C. The nanoparticles size value is given as an average of five measurements.

The molecular weight of the copolymers was determined by gel permeation chromatography (GPC) technique at ambient temperature. The system was equipped with an adjustable flow capacity and constant rate pump LC1120 type, and an evaporative mass detector PL-EMD 950 type, columns PL-gel 5 μ m MIXED-D, and PL-gel 5 μ m MIXED-C packed

TABLE I
Films Composition from PVA and PVA-g-LA Copolymers (C₁–C₃) With or Without Silver Nanoparticles

Films	VA/LA molar ratios	PVA aqueous solution, 10 wt % (g)	PVA-g-LA aqueous solution, 14 wt % (g)	Glycerol (mL)	Silver colloidal solution, 10 ⁻³ M (mL)	Sodium tetraborate solution, 5 wt % (mL)
PVA	1/0	20	–	0.167	–	0.20
PVA/Ag	1/0	20	–	0.167	0.746	0.20
C ₁	1/1	–	20	0.234	–	0.28
C ₁ /Ag	1/1	–	20	0.234	1.036	0.28
C ₂	1.5/1	–	20	0.234	–	0.28
C ₂ /Ag	1.5/1	–	20	0.234	1.036	0.28
C ₃	2.2/1	–	20	0.234	–	0.28
C ₃ /Ag	2.2./1	–	20	0.234	1.036	0.28

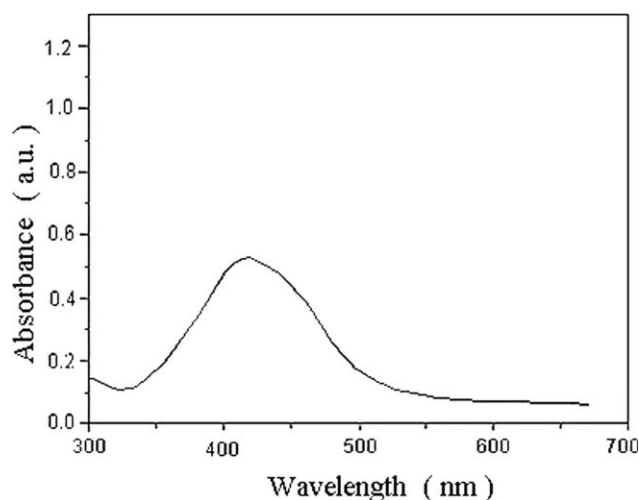


Figure 1 UV-vis absorption spectra of silver colloidal nanoparticles in water.

with polystyrene standards (molecular weight, 580–316,500). DMF was used as the mobile phase at a flow rate of 0.7 mL/min.

Differential scanning calorimeter (DSC) thermal analyses were carried out by means of a DSC Mettler 12E type (Switzerland) with heating rate of 10°C/min in nitrogen atmosphere. The first heating run was carried out with a 10- to 12-mg sample in the temperature range between room temperature and 250°C. The second heating run was recorded with the same sample that was rapidly cooled to room temperature and then heated again to 250°C. Pure indium was used as standard for calorimetric calibration.

The mechanical properties were determined using a dynamometer Tira-Test-2200 model (Germany) for tensile test with a tension speed of 30 mm/min. There were used test pieces with 100 mm × 10 mm ($L \times l$) dimensions, thickness comprised between 150 and 250 μm , and the active length of test piece was 50 mm. Before submitting to tensile test, the test pieces were thermostated 3 h in a vacuum oven at 50°C and residual pressure of 0.01 daN. The result was taken as an average value of five determinations for each sample.

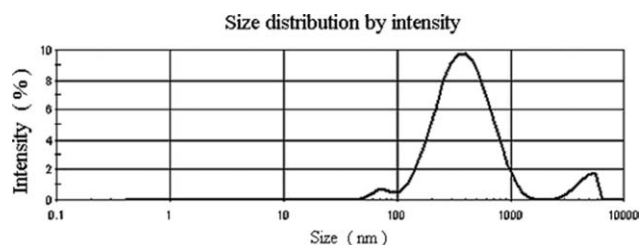


Figure 2 Size distribution by intensity of silver nanoparticles.

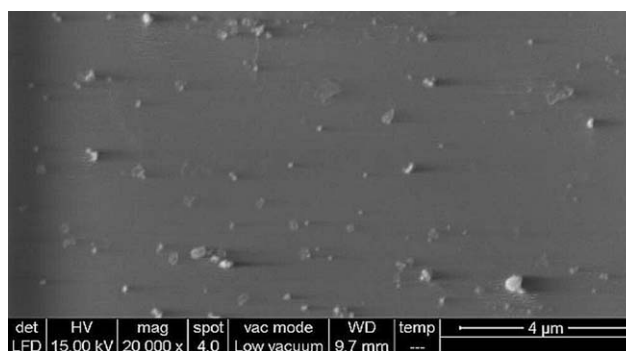


Figure 3 SEM of silver nanoparticles.

The dynamic mechanical analyses (DMA) were studied with a mechanodynamic analyzer, Perkin-Elmer Diamond Dynamical Mechanical Analyzer model. The films were cut as test pieces 15 mm × 10 mm × 0.2 mm ($L \times l \times h$) and analyzed on temperature range -100 and $+200^\circ\text{C}$, heating speed 2°C/min, and the oven was cooled with liquid nitrogen. The samples were analyzed at 1-Hz frequency and under tension mode. The storage modulus (E'), the loss modulus (E''), and $\tan \delta$ were recorded as a function of temperature.

To examine the antimicrobial behavior of the PVA/Ag and PVA-g-LA/Ag films, they were placed on agar-agar medium, inoculated with fungi, *Chaetomium globosum* class, MO 5 stock. The fungi were cultivated on Heynes medium (yeast extract, 4 g; malt extract, 10 g; dextrose, 4 g; agar-agar, 15 g; distilled water, 1000 mL), and after 7 days of seeding on these cultures the films were applied. Temperature was maintained at 28°C and monitoring was carried out for 14 days after films application on agar medium. The morphology of films was analyzed by SEM to study aspects of the surface. A scanning electron microscope (SEM)/ESEM-EDAX Quanta 200 model was utilized with 3-nm resolution and the accelerating tension varied between 10 and 30 kV.

RESULTS AND DISCUSSION

FTIR and ^1H NMR characterization

In Figure 4 are presented FTIR spectra of PVA-g-LA copolymer, obtained by the grafting reaction of PVA with LA and of the starting products (PVA and LA). In FTIR spectrum of LA, one can observe the presence of many absorption bands characteristic to hydroxyacids, the positions of these bands are in agreement with literature data.²⁰ At 3429 cm^{-1} exists a wide absorption band (νOH) that belongs to OH group at 2994 and 1044 cm^{-1} stretching vibrations characteristic to νCH_3 and $\nu(\text{C}-\text{CH}_3)$ aliphatic groups, respectively; at 1457 cm^{-1} are recorded

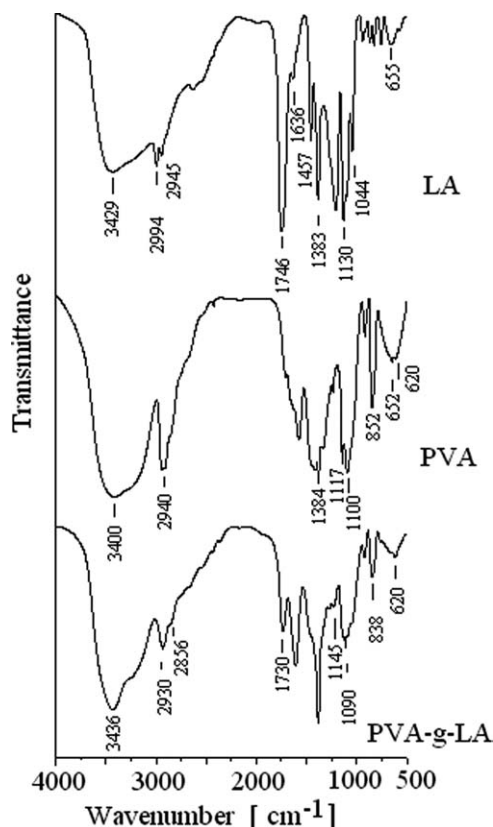


Figure 4 IR spectra: LA, PVA, and PVA-g-LA copolymer.

asymmetric deformation vibrations belonging to δCH_3 and at 1383 cm^{-1} deformation vibrations of δCH_3 and δOH bands. The carboxylic group that participates to the grafting reaction is noticed at 1746 cm^{-1} (νCOOH band), the H_2O bending peak appears approximately at 1636 cm^{-1} , and stretching vibrations ($\nu\text{C}-\text{OH}$) specific to secondary alcohols at 1130 cm^{-1} . In FTIR spectra of PVA-g-LA and PVA, the presence of some wide absorption bands νOH at $3400\text{--}3436\text{ cm}^{-1}$ characteristic to OH group and to intramolecular H linkages in polyols and at $1090\text{--}1145\text{ cm}^{-1}$ characteristic to $\nu\text{C}-\text{OH}$ groups in secondary alcohols are observed. In the domain $2856\text{--}2940\text{ cm}^{-1}$, the presence of alkyl bands is noticed: νCH , νCH_2 , νCH_3 , in PVA and LA. Referring to PVA polymer, absorption bands δOH at $1339\text{--}1384\text{ cm}^{-1}$ can be seen, while in the case of PVA-g-LA copolymer, these bands are missing or much decreased. Also the high intensity of absorption band $\nu\text{C}=\text{O}$ at 1730 cm^{-1} present in FTIR spectrum of PVA-g-LA copolymer belonging to ester COOR group confirmed that grafting reaction of PVA with LA took place. Bands at 620 and 652 cm^{-1} are assigned to out-of-plane vibration of the OH group, while the band at 852 cm^{-1} corresponds to the out-of-plane vibration of the CH group. It should be emphasized that the band attributed to the out-of-plane OH vibrations in alcohols is quite broad (from

620 to 750 cm^{-1}) and has high intensity.²¹ After the polyesterification reaction, the intensity of this band (observed in FTIR spectrum of the copolymer) lowers very much confirming that the OH groups of PVA participate at the reaction.

^1H NMR spectrum of PVA-g-LA copolymer is presented in Figure 5. Based on the reports of peak assignments for proton species in PVA and PVA derivatives,^{22–24} we assigned the proton signals in the ^1H NMR spectrum of PVA-g-LA copolymer as given in the figure. In the ^1H NMR spectrum of the copolymer, the resonance at $\delta = 1.299\text{ ppm}$ was attributed to the sequences of LA units CH_3 (d) grafted to PVA chain. The signal appearing at 1.415 ppm was assigned to the methylene protons CH_2 (a) existent in PVA backbone structure, the signal at 3.651 ppm was attributed to the methine proton CH (b) existent in PVA units, and the signal at 4.793 ppm to the methine proton CH (c) in LA unit of the graft copolymer. Residual proton signal of D_2O appeared at 4.238 ppm .

Molecular weight

The average molecular weights of $\text{C}_1\text{--}\text{C}_3$ copolymers determined by GPC had values between 34×10^3 and 53×10^3 and the polydispersity index (M_w/M_n) was between 1.251 and 1.368 (Table II) and varied with VA/LA molar ratio. The obtained copolymers had reduced polydispersity index, good solubility in water, DMF, and dimethylsulfoxide (DMSO). By LA percentage increase in the initial reaction mixture, a copolymer with higher molecular weight (C_1) was achieved due to participation in the reaction of more COOH groups from LA. In C_1 copolymer with VA/LA molar ratio 1/1 in reaction mixture, the amount of OH unreacted groups determined by the method described in Ref. 25 was lower (9.16 g OH/100 g copolymer), while for molar ratio 2.2/1 (copolymer C_3), the value was 13.10 g OH/100 g copolymer. The

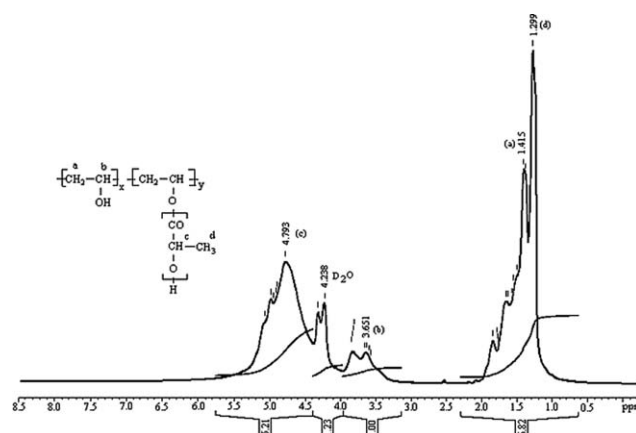


Figure 5 ^1H NMR spectrum of PVA-g-LA copolymer.

TABLE II
Average Molecular Weights of PVA and C₁-C₃ Copolymers Determined by GPC

Copolymer	M_n	M_w	M_w/M_n	g OH/100 g copolymer	Yield (%)
C ₁	53,000	73,156	1.368	9.16	68
C ₂	40,000	54,461	1.360	11.20	72
C ₃	34,000	42,739	1.251	13.10	76
PVA	18,000	32,600	1.810	38.64 ^a	-

^a Theoretical value.

high percentage of LA in the initial reaction mixture lead to bigger grafts length, thus contributing to copolymer molecular weight increase. Taking into account the quite large average molecular weights values of copolymers compared with PVA, we concluded that the grafting reaction took place.

Thermal analysis: TG and DSC

Thermal behavior of PVA and C₁-C₃ films, achieved with and without silver nanoparticles were studied by thermogravimetric analysis in the air. Weight losses determined by thermal oxidative decomposition are presented in Figures 6 and 7, and data on thermal stability and activation energies (E_a) in Table III. Thermogravimetric curves present three thermal decomposition processes that occur with different speeds. In the first process, absorbed moisture and small molecular compounds were removed. Most of the mass loss took place between 160 and 370°C, subsequently smaller mass loss followed before 550°C. The results were consistent with the literature report on unreacted acetate group elimination of polymer side chains at lower temperatures, followed by the polymer backbone breakdown at higher temperature.²⁶ Accordingly, the decomposition temperature of PVA-g-LA samples in the main degradation stage was higher than that of neat PVA,

indicating that PVA esterification with LA can improve PVA thermal stability, due to interaction between PVA backbone and the oligo-PLA grafted chains. The main thermal decomposition processes of copolymer films without silver nanoparticles with weight losses of 56.8–61.3 wt % were situated between 170 and 365°C, while in the case of films with silver nanoparticles, the weight losses were more reduced (53.2–54.8%), although the temperature range was near to the anterior one (160–370°C). Thermal stability of the copolymers decreased as the molar ratio VA/LA increased from 1/1 to 2.5/1 (molecular weight lowered from 53,000 to 34,000), and weight losses of 50 wt % (in the case of the three copolymers) were located on temperature interval between 297 and 308°C. On the other hand, in the case of pure PVA weight loss of 50 wt % was recorded at 285°C. Also, we can notice that films achieved with PVA and silver nanoparticles have lower thermal stability than C₁-C₃/Ag ones. In the case of PVA/Ag films, weight loss of 50 wt % was recorded at 270°C, while in the case of C₁-C₃/Ag ones, they were recorded on 295–305°C interval. Thermal behavior up to ~ 350°C is important, because it gives us some information about copolymers concerning melt processing. By PVA grafting with LA, the crystallinity and hydrophilic/hydrophobic balance in the copolymer structure was

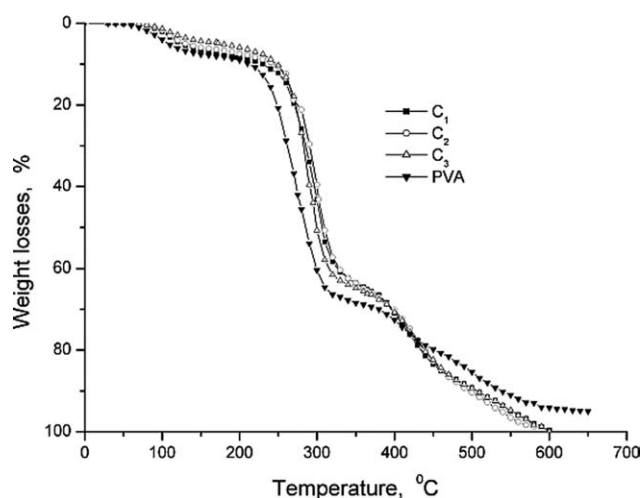


Figure 6 TG diagrams of PVA and C₁-C₃ films.

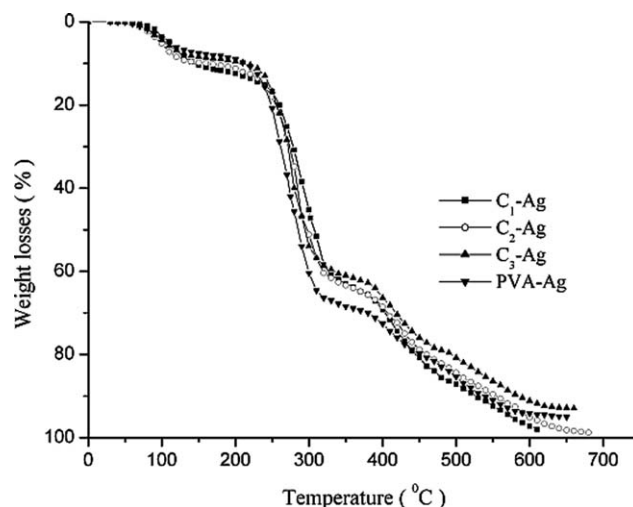


Figure 7 TG diagrams of PVA/Ag and C₁-C₃/Ag films.

TABLE III
Thermal Characteristics of PVA and C₁–C₃ Films by Thermogravimetric Analysis

Films	T ₁₀ (°C)	T ₅₀ (°C)	T _i (°C)	T _m (°C)	T _f (°C)	W _{T_i–T_f} (%)	E _a (kJ/mol)	n
PVA	165	285	160	275	370	61.6	99.68	1.5
C ₁	230	308	195	300	365	56.8	130.54	1.6
C ₂	245	307	170	302	365	59.0	78.40	0.7
C ₃	245	297	172	295	365	61.3	83.60	0.9
PVA/Ag	155	270	155	275	360	59.6	94.68	1.5
C ₁ /Ag	145	305	175	302	370	53.2	99.36	1.4
C ₂ /Ag	160	298	160	290	370	54.8	102.45	1.4
C ₃ /Ag	210	295	170	280	370	53.4	113.57	1.6

T₁₀, T₅₀, temperature corresponding to 10 and 50 % weight loss; T_i, T_f, the initial and ultimate temperature of the main thermal decomposition process; T_m, temperature corresponding to weight losses with maximum rate; W_{T_i–T_f}, weight losses on the T_i – T_f domain; E_a, n, activation energy and reaction order determined on the T_i – T_f domain.

modified, the molecular weight of copolymers increased 2–3 times, reported to PVA molecular weight and consequently the thermal stability of copolymers increased. Weight losses of 50 wt. % determined by thermal decomposition were situated around 300°C value much more raised than the melting and processing temperature of polymers. Gupta and Deshmukh²⁷ concluded that the carbonyl carbon–oxygen linkage is the most likely one to split by heating at elevated temperatures. The reactions involved in the thermal degradation of LA-based polymers are thermohydrolysis,²⁸ depolymerization,^{29–31} intermolecular and intramolecular transesterification.^{32–34}

Activation energies (E_a) and reaction order (n) were determined by Coats and Redfern³⁵ and Reich and Levi^{36,37} methods on T_i–T_f range (150–370°C), near the melting temperature and processing of copolymers (molded by hot pressing). In Figures 8 and 9, variation of E_a versus conversion degree of thermal decomposition processes analyzed on the temperature range T_i–T_f is presented. At the begin-

ning, the activation energies have large values and then decrease sharply with the outset of the thermal decomposition process. When conversion degree value increased over 0.10, the activation energies were stabilized and remained almost constant to the end of thermal decomposition process. The sudden decrease of the activation energies suggested that at the outset of the process, the decomposition reaction had an autocatalytic behavior, due to oxygen traces in copolymer structures that could have a catalytic effect on thermal decomposition processes. The activation energy dependence with the conversion degree is an indication that the samples have a complex thermal degradation mechanism in multiple steps of reaction.³⁸

Data obtained by DSC of films obtained from C₁–C₃ copolymers and PVA film doped with silver nanoparticles, as well as of ones without silver nanoparticles are presented in Table IV and Figure 10. From the data presented in the table, we can notice that the glass transition temperatures (T_g) of films achieved from C₁–C₃ copolymers have lower values,

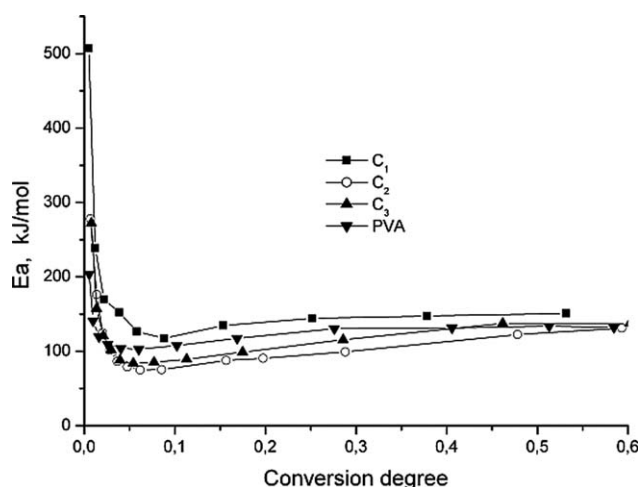


Figure 8 Dependence of E_a function of conversion degree of thermal decomposition processes of PVA and C₁–C₃ films.

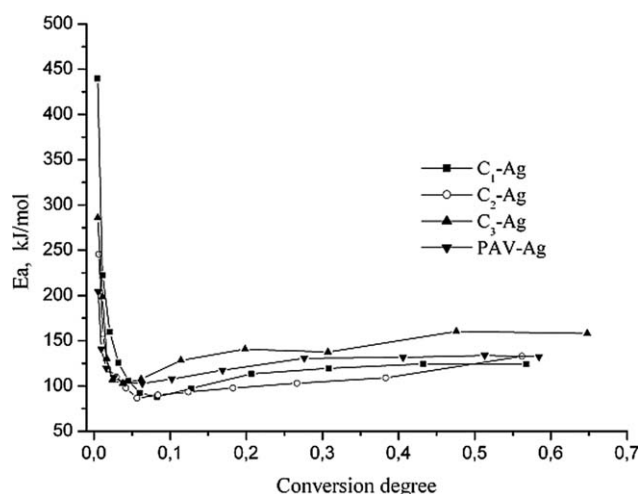


Figure 9 Dependence of E_a function of conversion degree of thermal decomposition processes of PVA/Ag and C₁–C₃/Ag films.

TABLE IV
Thermal Characteristics by DSC and DMA Analyses of PVA and C₁–C₃ Films With or Without Silver Nanoparticles

Sample	T_g^a (°C)	T_m^a (°C)	ΔH^a (J/g)	T_g^b (°C)	T_g^b (°C)
PVA	55	210	64.18	10.80	8.30
PVA/Ag	57	212	58.76	10.80	6.40
C ₁	54	172	14.00	14.30	18.30
C ₁ /Ag	50	170	13.00	7.96	9.84
C ₂	53	180	18.82	–	–
C ₂ /Ag	51	178	16.20	–	–
C ₃	53	195	35.07	20.77	19.65
C ₃ /Ag	52	193	32.42	19.43	16.10

^a Determined by DSC.

^b Determined by DMA.

–, undetermined values.

but close to T_g of PVA films. The slight decrease of T_g indicates that PVA-g-LA copolymers chains mobility was higher than of pure PVA, because oligo-PLA grafted chains decreased the strong intermolecular and intramolecular hydrogen bonds between or within PVA chains. In other words, as the oligo-PLA chains increase, their chain lengths and contents grafted into PVA macromolecular chains will become varied and diversify the extent of crystallization. These copolymers tended to be amorphous, which led to decrease of the melting temperature (T_m) and fusion heat (ΔH) values. Consequently, the melting temperatures of copolymer films (endothermic peaks) have lower values (170–195°C), comparative to PVA ones (210–212°C), but close to the melting temperature of semicrystalline PLA polymer (about 180°C).³⁹ As a result, PLA side-chains may serve as an effective “internal” plasticizer to PVA, and PVA-co-LA copolymers will have improved melt processing properties. In literature, it

is reported that nonplastified PVA has no melting temperature, it decomposes at 220°C, while in the plastified state (with water or glycerol and dependent on its conformation structure), the melting temperature varies between 210 and 250°C.⁵ Also, one can notice that T_m of films has a general increase tendency with VA/LA molar ratio increase. On the other side, the presence of silver nanoparticles in films composition determines an insignificant decrease of T_m ($\sim 2^\circ\text{C}$). The melting enthalpy was calculated from the melting peak area by integration, considering also the experimental recording conditions. The melting enthalpies of copolymer films have half decreased values, comparative to melting enthalpies of PVA ones. The presence of silver nanoparticles in the film composition determines a slight melting enthalpy decrease that varies between 2 and 6 J/g; also PVA ratio increase in the initial reaction mixture determined the melting enthalpy increase. The slight decrease of thermal parameters, in the case of films with silver nanoparticles can be due to the catalytic activity of silver. In temperature range 135–145°C, one can observe the presence of an endothermic peak that can result from plasticizer evaporation (glycerol), whose ignition temperature is $\sim 160^\circ\text{C}$.

Mechanical properties

The mechanical properties of films obtained with PVA and PVA-g-LA copolymers are presented in Figures 11 and 12. The tensile strength (Fig. 11) is 13.56 N/mm², in the case of PVA films without silver nanoparticles and 14.10 N/mm² for films with silver nanoparticles. The tensile strength of copolymer films has lower values comparative to PVA ones. The high inter- or intramolecular hydrogen bond force of neat PVA films determines a higher tensile strength comparative to PVA-g-LA ones, as the substitution of hydroxyl groups with polylactic acid oligomers can obviously hinder the formation of hydrogen bonds, due to grafted molecular

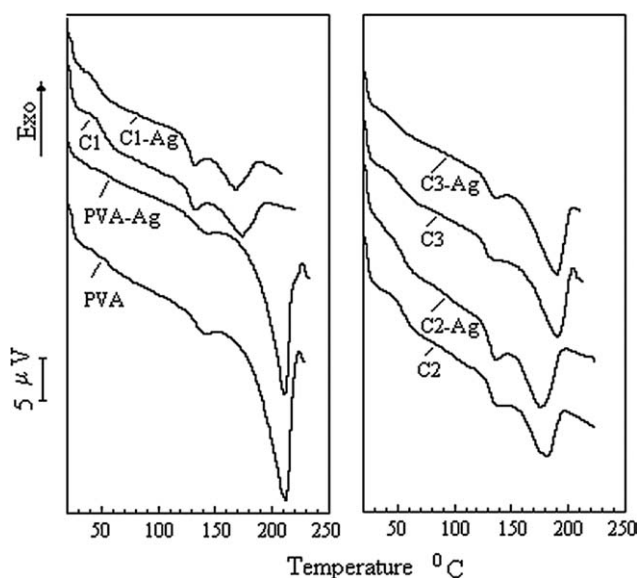


Figure 10 DSC curves of PVA and C₁–C₃ films with and without silver nanoparticles.

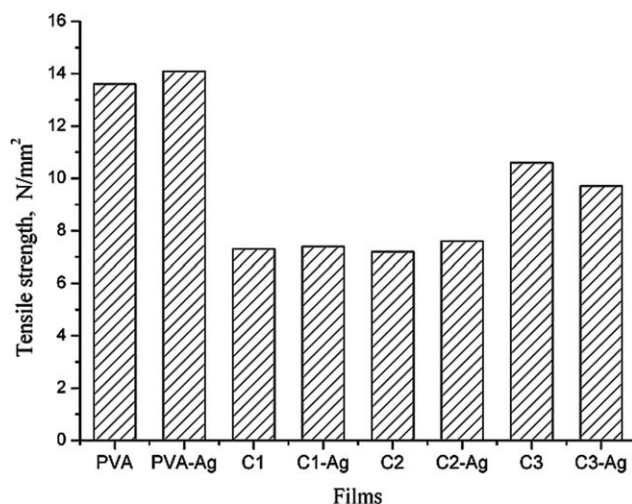


Figure 11 Tensile strength of PVA and C₁–C₃ films with and without silver nanoparticles.

structure. Concerning silver nanoparticles' influence on tensile strength of films prepared with PVA-g-LA copolymers, we can notice that this parameter does not record major modifications comparative to blank samples. Analyzing the influence of VA/LA molar ratio in copolymer structure, it was noticed that with VA molar ratio increase, the tensile strength had higher values but it did not exceed PVA films tensile strength. The films achieved using C₃ copolymer, with VA/LA molar ratio (2.2/1), have higher tensile strength value (10.50 N/mm²), comparative to the other ones. As silver nanoparticles were introduced in very low quantities (40 ppm reported to the polymers gravimetric weight), it was noticed that they could not modify the tensile strength. Generally, it was remarked only a slight increase of the tensile strength, indicating that there existed a good compatibility among components.

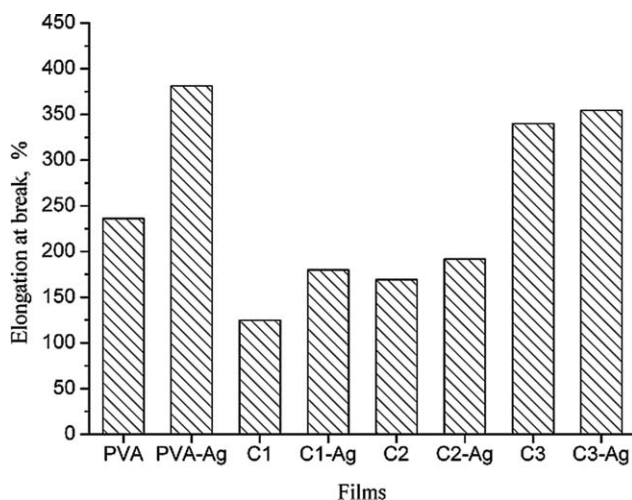


Figure 12 Elongation at break of PVA and C₁–C₃ films with and without silver nanoparticles.

Analyzing the influence of silver nanoparticles on films structure, it was noticed that in all cases the elongation at break (Fig. 12) recorded an increase, the most important one was in the case of PVA/Ag films (381%), comparative to PVA ones (236%). Concerning the influence of VA/LA molar ratio in the initial mixture utilized in copolymers synthesis, it was noticed the same tendency as in the case of tensile strength, namely the VA molar ratio increase determined the elongation at break increase. In the case of films achieved with C₃ copolymer, the elongation at break presented even more raised values comparative to PVA one (blank sample). Generally, the elongation at break values of films varies between 125 and 381% and can be influenced by plastifying with glycerol. The plastifying agent weakens temporarily the intermolecular interaction forces and subsequently facilitates lubrication of the macromolecular chains. Simultaneously, by plasticizer introduction, beside the reduction of the potential barrier of intern rotation, a plasticity increase is achieved that helps processing and lowers the elasticity modulus.

Thermomechanical properties

The thermomechanical properties of films achieved with PVA and copolymers were studied by mechanodynamic analysis, and results are presented in Figures 13 and 14, and Table IV. In the study, films of PVA, C₁ and C₃ copolymers were used with and without silver nanoparticles. The storage modulus (E') had more raised values in the case of films achieved with copolymers. The relaxation processes temperature (T_α), for the studied films was determined as the maximum value of peaks $\tan \delta$, and the glass transition temperature (T_g) was taken at middle of glass transition processes, situated on the

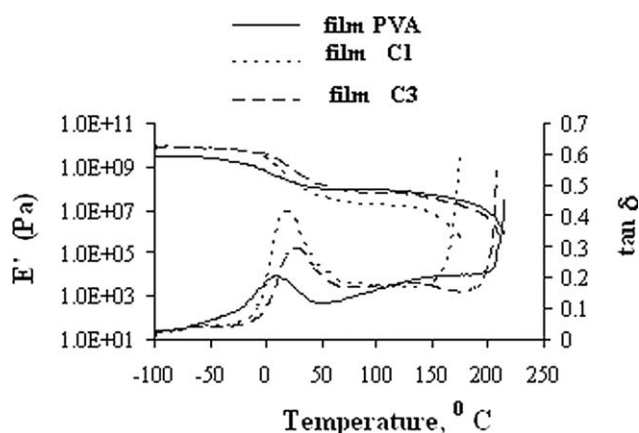


Figure 13 Variation of storage modulus (E') and of dissipation factor ($\tan \delta$) with temperature at films without silver nanoparticles.

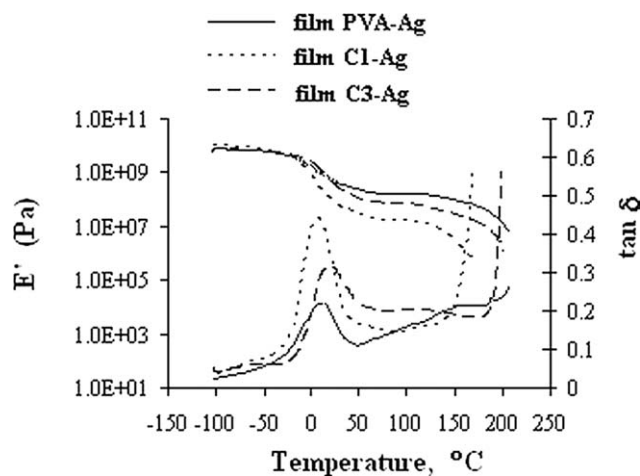


Figure 14 Variation of storage modulus (E') and of dissipation factor ($\tan \delta$) with temperature at films with silver nanoparticles.

curve of storage modulus. The curves of the storage modulus E' , in the case of films achieved with PVA and copolymers with or without Ag° nanoparticles presented a single transition process on temperature range -100°C to $+200^{\circ}\text{C}$. Generally, the storage modulus decrease was produced in the region of glass transitions situated between 6 and 20°C . The T_g values are comprised between 8.30 and 19.60°C , in the case of films without Ag° nanoparticles and between 6.40 and 16.10°C for films with Ag° nanoparticles, and they vary with copolymers composition (Table IV). The T_g values determined by DMA were lower comparative to those obtained by DSC, as in this case the films were dried under vacuum at 80°C and in the case of DMA analyses, the films were stored at 5 – 7°C to avoid the plastifying agent migration. The presence of glycerol determined an important lowering of the T_g value and films presented elasticity at ambient temperature. In the case of copolymer films, the values of the relaxation processes (T_{α}) and T_g values were more raised comparative to corresponding PVA ones (except T_g value of C_1/Ag film). These values are influenced by VA/LA molar ratio utilized in the syntheses, considering that with LA percent decrease, the values of these two parameters record an increase. The slope of the glass transition processes (E' modulus curve) had higher values in the case of copolymers comparative to PVA and recorded a raised value in the case of copolymer with VA/LA (1/1) molar ratio. This reality demonstrates that the beginning and the end of the transition process is nearer and consequently the glass transition domain narrower. The same behavior was also observed in the case of the dissipation factor ($\tan \delta$), when the peak is narrow and higher in the case of copolymers, supporting the anterior statement.

Antibacterial testing

The films surface was examined by SEM after maintaining PVA and PVA-g-LA films on agar medium inoculated with fungi *Chaetomium globosum* class, MO 5 stock for 2 weeks. In Figure 15(a,b), PVA and PVA/Ag films are presented. PVA matrix presents a homogeneous and uniform structure constituted of a single phase. On the surface of the film without silver nanoparticles, the appearance of hives belonging to *Chaetomium globosum* class fungi is observed; on the contrary, in the case of films with silver nanoparticles one can observe the presence and dispersion of silver nanoparticles on the films surface and the absence of fungi or other bacterial species, demonstrating the bacteriostatic character of these films.

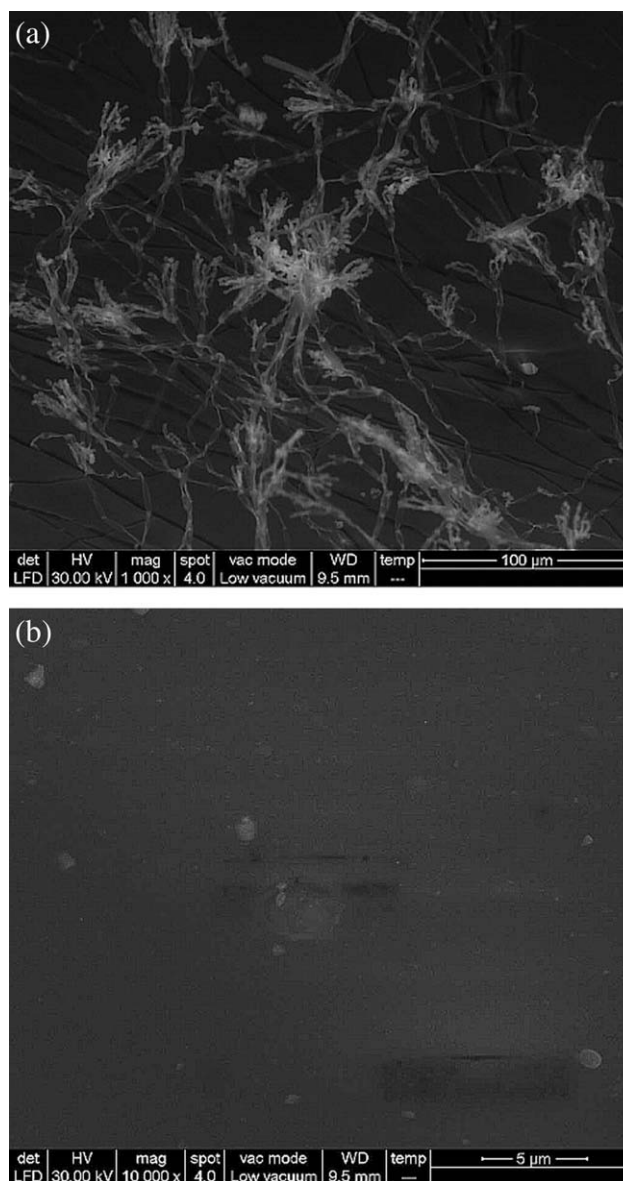


Figure 15 (a) SEM micrographies of PVA films and (b) SEM micrographies of PVA/Ag films.

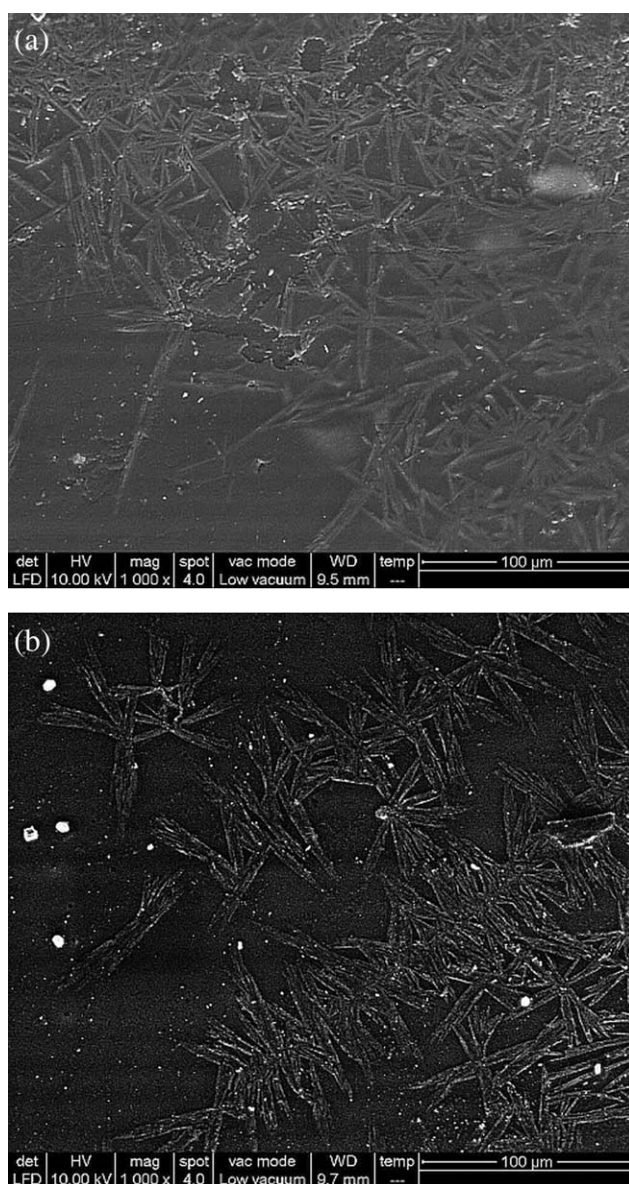


Figure 16 (a) SEM micrographies of PVA-g-LA films and (b) SEM micrographies of PVA-g-LA/Ag films.

The appearance of the fungi hives on the films surface without silver nanoparticles was observed after 4–5 days on agar application, while in the case of films with silver nanoparticles, they were not developed even after 14 days. SEM micrographies [Fig. 16(a)] belong to PVA-g-LA (C_1) film without silver nanoparticles, and Figure 16(b) to films with silver nanoparticles. In this case, one can observe that the structure of the films is not homogeneous, formed by two phases characteristic to the two types of structural unities. The homogeneous and uniform part is characteristic to PVA units and the heterogeneous one, as short fibers dispersed in the mass belongs to oligo-PLA chains. The surface of PVA-g-LA films without silver nanoparticles presents cracks and an advanced degree of erosion resulted by the

action of the fungi; in the case of films with silver nanoparticles, the surface is not attacked by *Chaetomium globosum*, demonstrating their bacteriostatic character.

CONCLUSIONS

By PVA grafting with L(+)-LA, copolymers with water solubility and in some organic solvents (DMF, DMSO, acetone, and ethyl ether) and better thermal stability were achieved. The PVA-g-LA synthesized compounds exhibit lower glass transition and melting temperature and higher decomposition one than neat PVA; therefore, they could also be utilized to prepare some films by melt processing. The copolymer films achieved presented bacteriostatic activity against *Chaetomium globosum* fungi, when we included in their composition silver nanoparticles. The appearance of the fungi hives on the films surface without silver nanoparticles was observed after 4–5 days on agar medium application, while in the case of films with silver nanoparticles they were not developed even after 14 days. The fact that silver nanoparticles introduced in small quantities did not modify the thermal and mechanical properties of copolymer films and even determined their easy improvement, as well as the antimicrobial character that was noticed could determine their possible utilization in the medical and pharmaceutical field. The films were prepared by solution casting from aqueous solutions, and the mechanical properties were not essentially modified, the values recorded remained in the domain of films achieved with PVA blank sample.

The raw materials used in the syntheses (LA and PVA) are biodegradable and biocompatible and suggest copolymers utilization in various areas: packaging, agriculture, medicine, pharmacy (controlled release systems of some active principles, surface coatings, and antiseptic dressings), considering also their bacteriostatic character, given by silver nanoparticles. Moreover, the use of LA for PVA graft copolymerization presents some other advantages: LA is not only easily available from renewable resources but has also low cost. Therefore, PVA-g-LA is a useful biomaterial from environmental and economical point of view.

References

1. Gimenez, A.; Mantecon, J. C.; Cadiz, V. *J Appl Polym Sci* 1997, 65, 1643.
2. Arranz, F.; Sánchez, C. M.; Gil, F. *Die Angew Makromol Chem* 1980, 92, 121.
3. Tudorachi, N.; Lipsa, R. *Material Plast* 2004, 41, 99.
4. Carlotti, S. J.; Beaune, O. G.; Schué, F. *J Appl Polym Sci* 2001, 80, 142.

5. Finch, C. A. *Polyvinyl Alcohol Properties and Applications*; Wiley: Bristol, Great Britain, 1973.
6. Inotte, Y.; Yoshie, N. *Prog Polym Sci* 1992, 17, 571.
7. Duda, A.; Penczek, S. *Polimery (Warsaw)* 2003, 48, 16.
8. Hayashi, P. *Prog Polym Sci* 1994, 19, 663.
9. Libiszowski, J.; Kowalski, A.; Biela, T.; Duda, A. *Polimery (Warsaw)* 2004, 49, 690.
10. Dritch, E. A.; Marino, A. A.; Malakanok, V.; Albright, J. A. *J Trauma* 1987, 27, 301.
11. Terry, R. N. Brevet USA 6,716,895 B1 (2004).
12. Shin, H. S.; Yang, H. J.; Kim, S. B.; Lee, M. S. *J Colloid Interface Sci* 2004, 274, 89.
13. Garell, L. R. *Anal Chem* 1989, A61, 401.
14. Jain, P.; Pradeep, T. *Biotechnol Bioeng* 2005, 90, 59.
15. Russell, A. D.; Hugo, W. B. *Progr Med Chem* 1994, 31, 351.
16. Tudorachi, N. *e-Polymers* 2008, 131, 1.
17. Qiu, Y.; Lally, J. M. WO 2005/014074 A1.
18. Lee, P. C.; Meisel, D. *J Phys Chem* 1982, 86, 3391.
19. Al-Rawashdeh, N. A. F.; El-Akhras, A. I.; Abbo, M.; Al-Mubarak, M. O. J. *J Chem* 2008, 3, 57.
20. Chen, Y. K.; Lin, Y. F.; Peng, Z. W.; Lin, J. L. *J Phys Chem C* 2010, 114, 17721.
21. Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1998, pp 85–90.
22. Liu, Y.; Yuan, M.; Deng, X. *Eur Polym Mater* 2003, 39, 977.
23. Gong, Q.; Wang, L. Q.; Tu, K. *Carbohydr Polym* 2006, 64, 501.
24. Ding, J.; Chen, S. C.; Wang, X. L.; Wang, Y. Z. *Ind Eng Chem Res* 2009, 48, 788.
25. Sander, B.; Ziegler, H. J.; Bischof, C. *Die Angew Makromol Chem* 1990, 181, 171.
26. Ballistreri, A.; Foti, S.; Montaudo, G.; Scamporrino, E. *J Polym Sci: Polym Chem Ed* 1980, 18, 1147.
27. Gupta, M. C.; Deshmukh, V. G. *Colloid Polym Sci* 1982, 260, 514.
28. von Open, R.; Michaeli, W. *Clin Mater* 1992, 10, 21.
29. Södergård, A.; Näsman, J. H. *Polym Degrad Stab* 1994, 46, 25.
30. Jamshidi, K.; Hyon, S. H.; Ikada, Y. *Polymer* 1988, 29, 2229.
31. Zhang, X.; Wyss, U. P.; Pichora, D.; Goosen, M. F. A. *Polym Bull* 1992, 27, 623.
32. Tighe, B. J. *Dev Polym Degr* 1984, 5, 31.
33. Garozzo, D.; Giuffrida, M.; Montaudo, G. *Macromolecules* 1986, 19, 1643.
34. Kopinke, F. D.; Remmler, M.; Mackenzie, K.; Möder, M.; Wachsen, O. *Polym Degrad Stab* 1996, 53, 329.
35. Coats, W. A.; Redfern, P. J. *Nature* 1964, 68, 201.
36. Reich, L.; Levi, W. D. *Makromol Chem* 1963, 66, 102.
37. Reich, L.; Levi, W. D. *Encyclopedia of Polymer Science and Technology*, vol. 14; Wiley-Interscience: New York, 1971.
38. Opferman, J. *J Therm Anal Cal* 2000, 60, 641.
39. Sodergard, A.; Stolt, M. *Prog Polym Sci* 2002, 27, 1123.