Effect of Nanosilver on the Photodegradation of Poly(lactic acid)

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ABSTRACT: The poly(lactic acid), PLA, mixed with nanosilver in solution easily forms nanocomposite in solid state (after solvent evaporation), which was proved by UV–Vis spectroscopy. This work focuses on photodegradation occurring in PLA films doped with nanosilver. The changes in chemical structure of photodegraded PLA has been determined using FTIR spectroscopy. Differential scanning calorimetry of UV-irradiated PLA samples provided information on polymer glass transition and crystallization/melting processes. It was found that PLA alone is more sensitive to photodegradation than PLA/silver nanocomposites. The mechanism of nanocomposite photodegradation and effect of nanosilver was discussed. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40144.

INTRODUCTION

Biodegradable polymers, particularly from renewable resources, have attracted much attention in the recent years because they are good alternative to synthetic plastics produced from petroleum.[1–5] Among them, poly(lactic acid) (PLA) becomes very popular, and it finds wide applications (e.g., in packaging industry, in medicine and pharmacy). PLA is produced from lactic acid or cyclic lactide, its manufacturing technology and processing is well known. The structure and properties of PLA have been intensively studied[2,4–8] but there is still a lack of information on its behavior in the presence of silver nanoparticles applied as antibiocidal agent. From practical point of view, photochemical and thermal stability of material based on PLA is also important, particularly when it has to be used at elevated temperature or exposed to electromagnetic radiation. The degradation in polymers is very complex and numerous factors influence this process: temperature, light, atmosphere, humidity, presence of internal and external impurities, thermal or photochemical catalysts or sensitizers.

Even if the physicochemical properties and susceptibility to degradation of virgin polymers are known, it is necessary to investigate them in composition with additives and modifiers. The mutual interactions between degradation products formed in each component can significantly change the course of decomposition in the blend or composite.

PLA outdoor applications in replacing conventional petrochemical-based polymers would be seriously limited because sunlight is the principal source of ultraviolet (UV) irradiation, and the degradation of PLA would be strongly accelerated by UV exposure. Therefore, the UV-resistance properties of PLA have to be reinforced for its commercialization of daily products. Usually, chemical absorbing agents are used to improve the UV-resistance properties of plastics, but these chemical compounds are usually toxic to human health and they may migrate during the storage and use of products. Therefore, alternative processes are expected for improving the stability of PLA under UV exposure.

The photo-oxidation of PLA composites with different types of particles was intensively studied in last years. Bocchini and Frache[9] studied the effect of organically modified montmorillonite and micro-talc on photo-oxidation of polylactide. The addition of filler increases the anhydride formation rate; this increase depends on the size/type of filler and on iron concentration. Nanoparticles such as clays, with a high interfacial area and high iron concentration increase the PLA photo-oxidation to two orders of magnitude. The stability of PLA/TiO$_2$ nanocomposite under UV irradiation was also studied. Optical measurements indicated that PLA chains would be broken to generate new carboxyl groups and other photoproducts under UV irradiation in presence of eater, and TiO$_2$ particles have a UV-screening effect.[10] Other authors suggest that photodegradability of nanocomposites can be efficiently promoted through the incorporation of TiO$_2$ nanoparticles, and the photodegradation rate of PLA/TiO$_2$ nanocomposites can be controlled by TiO$_2$ nanoparticles content.[11] Recent studies conducted by

Gorrasi and Sorrentino[12] on photodegradation of PLA with carbon nanotubes show that inclusion of conducting carbon nanotubes improves the stability of PLA.

The aim of this work was to study the photochemical degradation of novel PLA films doped with nanosilver especially from point of their molecular and chemical structure.

The addition of Ag nanoparticles to PLA matrix allows to obtain antibacterial properties of the composite[13] (and references cited herein), which can be applied in medicine and pharmacy. In such applications, the effect of short-wavelength radiation on material is a very important problem, and UV is often used for sterilization and disinfection.The photoinduced changes of physicochemical properties of PLA/Ag nanocomposite films have been studied by FTIR spectroscopy and differential scanning calorimetry (DSC) analysis.

EXPERIMENTAL

Materials

PLA (D-lactate content <1%), was supplied by Hycail (Netherlands). The dichloromethane (pure for analysis, POCh, Poland) was used as the polymer solvent. Nanosilver powder, particles size <100 nm, organically coated using polyvinylpyrrolidone (less than 0.2%, for dispersion in polar solvents), was obtained from Aldrich Chemistry.

Preparation of Samples

PLA/Ag nanocomposites were prepared by repeated mixing (ultrasonic and mechanical) of 4% (wt) PLA solution in dichloromethane with proper amount of nanosilver particles (previously dispersed in dichloromethane using ultrasounds). Thin polymeric films with thickness of 10 μm (and for chain scission observation—weak band at 868 cm^{-1} in FTIR spectrum—also 30 μm) were obtained by solution casting onto glass plates and solvent evaporation. The obtained films were then carefully dried for 4 h at 50°C. The weight fraction of silver in the PLA composites was 0.2% and 0.5%.

Photodegradation Conditions

The samples of pure PLA and PLA/Ag nanocomposites have be exposed to UV lamp produced by BakMed Lodz, type LB-151.1 (emitting 254 nm radiation) at ambient temperature (25°C). Maximum time of exposure was 60 h. After defined period of exposure time, the polymeric films were systematically analyzed by FTIR spectroscopy and DSC measurements.

FTIR Spectroscopy

Infrared spectra were recorded by Genesis II FTIR spectrometer (Mattson). For spectra analysis, WinFirst software (Mattson) was applied. The absorbances of selected bands were measured, and the relative change was calculated. The difference spectra of PLA and PLA+0.5% Ag before and after 60 h photodegradation was obtained.

UV–Vis Spectroscopy

The UV–Vis spectra of PLA and PLA with nanosilver were obtained using Spectrophotometer Jasco V-1630.

DSC

DSC measurements have been performed at air atmosphere using METTLER FP90 apparatus. The samples were heated with heating rate of 10°/min at 30–200°C range.
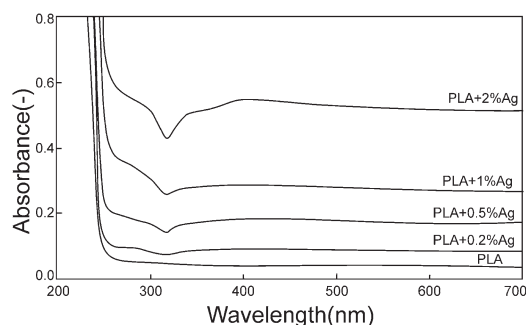

Figure 1. UV–Vis spectrum of PLA and PLA/nanosilver composites.

Mechanical Properties

Tensile test was carried out to determine the ultimate tensile strength, Young's modulus, and elongation at break using the Instron 5325 apparatus at room temperature. The testing was carried out at a rate of 5 mm/min with sample thickness of around 30 μm. At least five specimens were tested for each sample to get an average value.

Atomic Force Microscopy

Atomic Force Microscopy (AFM) measurements were done under the ambient air conditions using the NanoScope III, Digital Instruments with the silicon nitride tips (SiN$_3$). The contact mode was applied. The sensitivity of the tip deviation and the scanner resolution was smaller than 1 Å.

RESULTS AND DISCUSSION

Characteristics of PLA/Ag Compositions

Solutions of the composites and in the form of thin solid films were homogeneous and transparent. The PLA/Ag compositions were colorless, however for more than 1% Ag became slightly colored. Low intensive, broad absorption band at 320–450 nm was observed in UV–Vis absorption spectra (Figure 1). The presence of such absorption band is typical for polymer–silver nanocomposites.[13] Moreover, whole spectrum is moving to higher value of absorbance with increasing amount of nanosilver particles. It is evident from spectra that this effect in not caused by higher absorption of specimen but it is due to very efficient light scattering observed as increase of background in spectrum range.

Figure 2 shows an example of AFM photos of PLA+1% Ag nanocomposite. These images indicate the relatively uniform distribution of Ag nanoparticles within polymeric films but their size varies from few tens to about 100 nm. The shape of nanoparticles is generally spherical, however, some of them are nonspherical or form randomly distributed clumps.The photochemical degradation causes some visual changes, the films become more brittle.

FTIR Results of UV-Irradiated PLA and PLA/Ag Nanocomposites

Figure 3 presents FTIR spectrum of pure PLA without Ag additive (before and after 60 h of photodegradation). The main bands typical for PLA are: 2997 and 2946 cm^{-1}(C—H asymmetric and symmetric stretching vibrations), 1456 cm^{-1} (—CH$_3$ asymmetric bending vibration), 1382 cm^{-1} (C—H symmetric

Figure 2. AFM photos (recorded as height, phase, and amplitude images) of PLA+1% Ag nanocomposite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bending vibration), 868 cm^{-1} (C—C stretching vibration). Moreover, the intensive carbonyl bands C=O at 1756 cm^{-1}, C—O—C at 1190 (asymmetric) and 1093 cm^{-1} (symmetric) stretching vibration as well as weak hydroxyl band at 3500 cm^{-1} are present.[2] In early stages of exposure, the alterations of spectra in all cases are negligible (induction period). The marked changes appeared after longer time of irradiation.

For better observation of small spectral changes in exposed samples, the difference spectra were obtained. An example of such spectrum for PLA+0.5% Ag after 60 h of exposure is shown in Figure 4.

As can be seen, the large decrease of bands attributed to C=O (at 1756 cm^{-1}) and C—O (at 1190 and 1093 cm^{-1}) stretching vibrations was found. It obviously indicates the polymer photolysis. Simultaneously, the clear band at 1725 cm^{-1} is formed, suggesting the creation of new carbonyl groups in PLA. Moreover, low intensive band components were found at 1845 and 1645 cm^{-1}, which can be attributed to peracid/perester groups and double bonds (probably at the chain ends), respectively.

Figure 5(a–c) present the kinetic curves of photochemical processes occurring in thin films of PLA and its nanocomposites obtained on the base of the relative absorbance changes (A_t/A_0) of selected bands (at 1129, 1190, and 1756 cm^{-1}). It is clearly seen that the rate and efficiency of PLA photodegradation depends on the amount of Ag nanoparticles introduced to thin polymer film. Already 0.2% Ag significantly retards PLA photolysis and 0.5% Ag content further enhances this effect. The

induction periods (τ_i) determined from these curves are listed in Table I. Ag nanoparticles causes increase of τ_i above two or three times.

Simultaneous drop of absorbance at 868 cm^{-1} (weak band) attributed to —C—C— skeletal vibrations confirms that chain scission is dominant photoprocess. In thin samples (10 μm), the changes of absorbance in a range 868 cm^{-1} corresponding to —C—C— vibration are not easy to detect. Therefore, FTIR studies on thicker samples (30 μm) were performed to confirm that due photodegradation chain scission take place. Relative changes of absorbance in 868 cm^{-1} range (chain scission) are present in Figure 6. The main chain scission process was proved also by viscometric studies (not shown). The drop of limiting viscosity number after UV-irradiation is similar in both samples: PLA and PLA+Ag. As has been recently reported, the PLA photodegradation proceeds by homogeneous noncatalytic random degradation.[14] Moreover, UV-irradiation causes the racemization of monomeric products resulting to photoinduced tautomerization.

DSC Results of UV-Irradiated PLA and PLA/Ag Nanocomposites
DSC results of UV-irradiated PLA and PLA containing 0.5% Ag nanoparticles are shown in Figures 7 and 8. All curves exhibit the glass transition (with endothermic depression corresponding to relaxation processes), cold crystallization, and melting of PLA. Pure PLA has T_g of 62.5°C. The one broad crystallization peak in the range of 100–130°C is typical for PLA analyzed in

Figure 3. FTIR spectrum of PLA before and after photodegradation.

Figure 4. Differential spectrum for PLA and PLA+0.5% Ag in the range of 2000–500 cm^{-1} for 0–60 h of photodegradation.
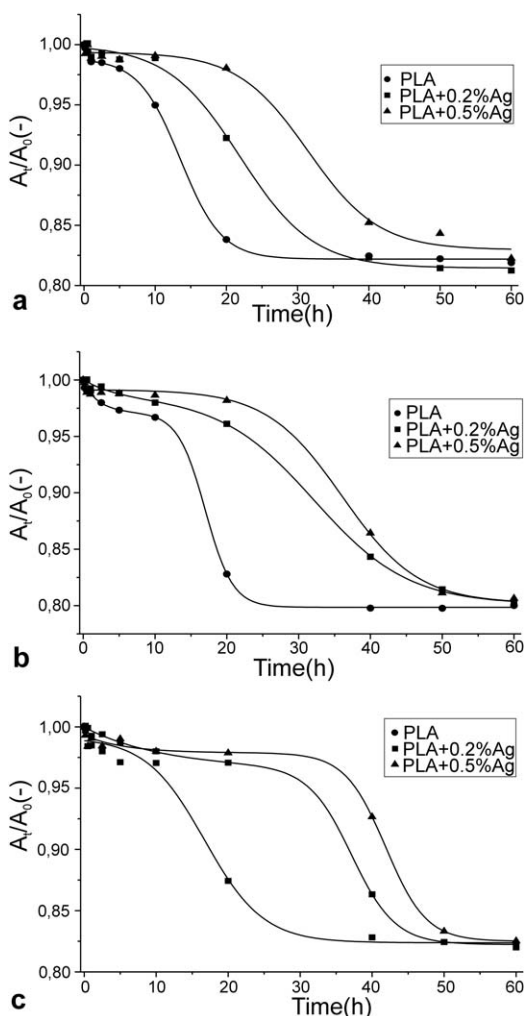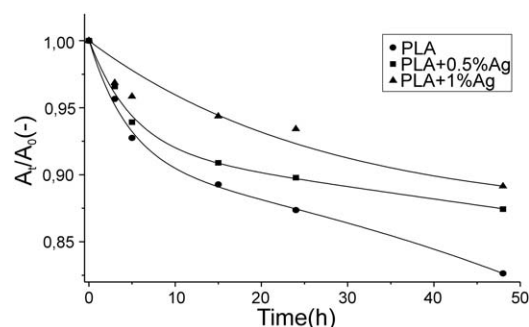
Figure 5. Relative changes of absorbance A_t/A_0 of selected bands from FTIR spectra of PLA and its composites with 0.2% and 0.5% content of nanosilver: (a) C=O (at 1756 cm^{-1}), (b) C—O (at 1187 cm^{-1}), and (c) —CH$_3$ (at 1129 cm^{-1}) versus irradiation time; film thickness: 10 μm; A_0 and A_t are absorbances of unirradiated specimen and after t time of exposure, respectively.

this conditions.[15,16] It is named "cold crystallization," which appears not from the melt but from the glassy state.

Interestingly, the single melting peak found in DSC curve for unexposed PLA (at 147.4°C) undergoes splitting in UV-irradiated samples (already after 5 h exposure). Both peaks (T_{m1}

Table I. Induction Period (τ_i, h) of Photochemical Degradation in PLA and PLA Containing Ag Nanoparticles Determined from FTIR Spectra

Band at wavenumber (cm^{-1}		τ_i (h)	
	PLA	PLA + 0.2% Ag	PLA + 0.5% Ag
1129	10	25	32
1187	10	20	28
1756	6	12	18

Figure 6. Relative changes of absorbance A_t/A_0 of —C—C— band (868 cm^{-1}) from FTIR spectra of PLA and its composites with 0.5% and 1% content of nanosilver versus irradiation time; film thickness: 30 μm; A_0 and A_t are absorbances of unirradiated specimen and after t time of exposure, respectively.

and T_{m2}) are not well separated and the difference between their positions on DSC curve is 3°–6°. This clearly indicates that at least two different types of crystals exist in UV-irradiated PLA.[17] It can be supposed that photodegradation leads to main chain scission and formation of shorter PLA fragments undergoing molecular reorganization. Short chains are characterized by higher mobility, thus, this new orderliness of partially decomposed polymer influences the melting process observed by DSC. The double crystalline peaks in PLA were described in literature as corresponding to crystallites of different size, various perfection or stability.[18–20]

The temperatures of phase transitions (T_g, T_{m1}, and T_{m2}) as well as enthalpies of crystallization and melting (ΔH_c and ΔH_m) in PLA, obtained from DSC curves, were plotted versus time of irradiation (Figures 9 and 10). It is clear that both glass and melting temperatures decrease with irradiation time (Figure 9). The observed changes are somewhat lower in PLA/Ag
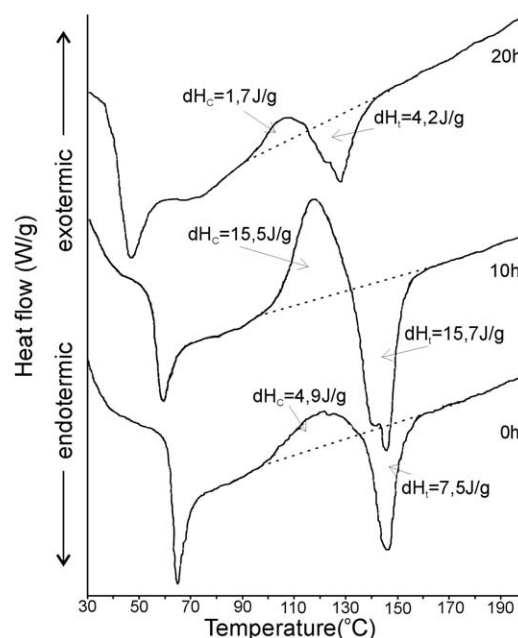
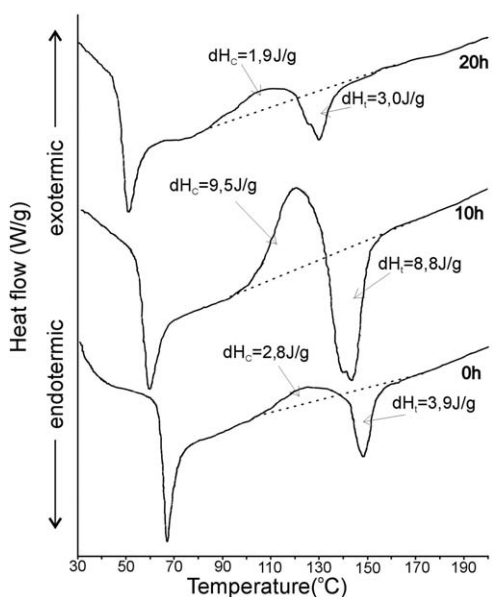**Figure 7.** DSC curves of PLA during different time of photodegradation.

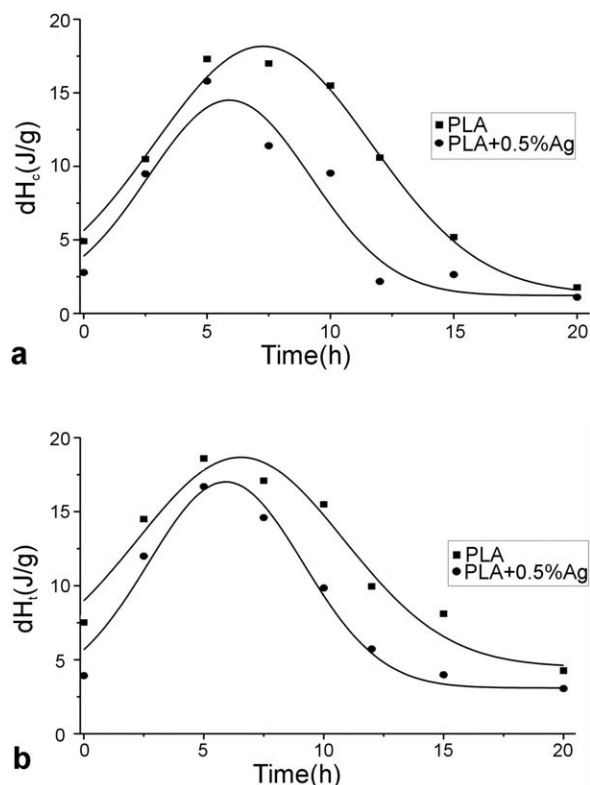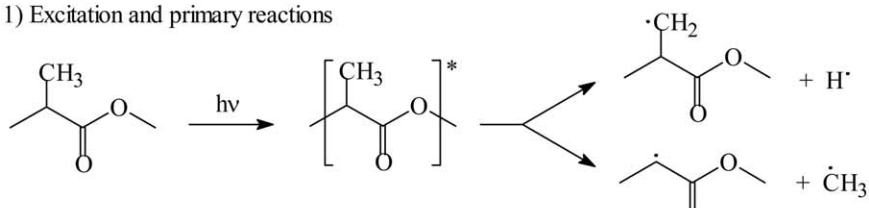**Figure 8.** DSC curves of PLA+0.5% Ag during different times of photodegradation.

Figure 10. Changes of crystallization, ΔH_c (a) and melting enthalpies ΔH_m (b) during photodegradation of PLA and PLA+0.5% Ag.

nanocomposites than those in pure PLA. It can be explained by the decrease of average molecular weight of PLA and formation of the low-molecular weight products, which plastify polymer and, moreover, they change the macromolecular order. The decrease of T_g in degraded PLA was also attributed to reduction of molecular weight by other authors.[21]

It is clearly seen, that the enthalpy of melting (ΔH_t) and crystallization (ΔH_c) have similar values. It means that here a cold crystallization influences on PLA crystallinity and observed enthalpy of melting. Enthalpy of melting and crystallization increases after the beginning of exposure, reaches maximal value between 5 and 10 h of sample irradiation, then again decreases (Figure 10). It indicates that initial degradation leads to better ordered macromolecule structure. However, prolonged exposure causes the drastic degradation leading to molecular chain scission and noticeable disorder. The enthalpy values observed in PLA are somewhat higher than in the case of PLA/Ag nanocomposite but the trend of changes is the same.

Mechanical Properties

The results of mechanical properties for PLA and PLA+1% Ag samples with thickness 30 μm indicate that the presence of nanosilver reduces Young's modulus (from 2900 to 2100 MPa), elongation at break (from 0.036 to 0.031 mm/mm), and ultimate tensile strength (from 55 to 45 MPa). The changes of mechanical properties caused by a 5 h of photodegradation are much larger in a case of neat PLA than in nanocomposites PLA+1%Ag. After 5 h of photodegradation of pure PLA, the Young's Modulus increases at 21%, but elongation at break and ultimate tensile strength decrease at about 90% (the samples are very brittle). In a case of nanocomposites with Ag the Young's modulus increases at about 100%, elongation at break decreases at about 60% but there are no changes in ultimate tensile
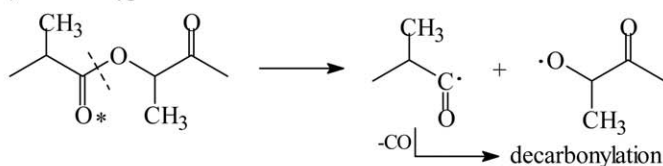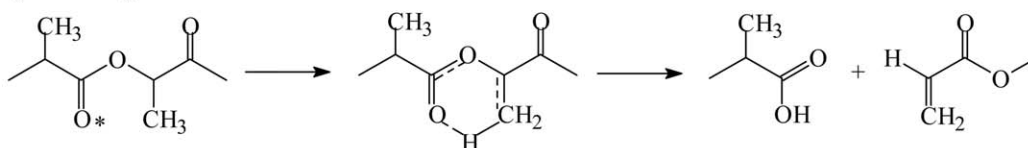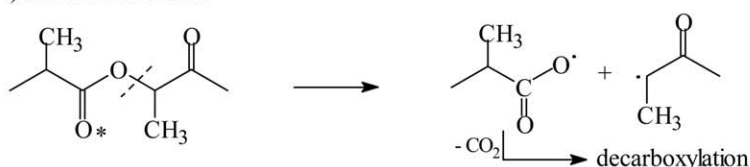

Figure 9. Dependence of glass transition, T_g (a) and melting temperatures: T_{m1} and T_{m2} (b) of PLA and PLA+0.5% Ag on irradiation time.
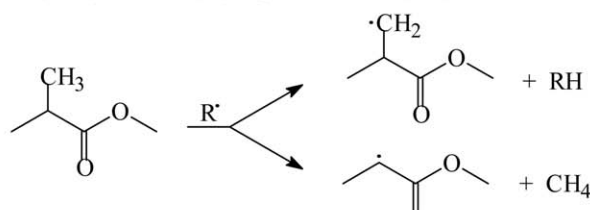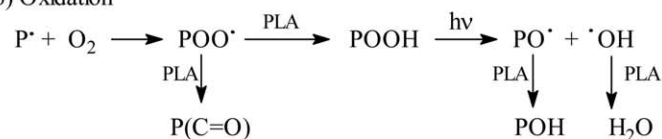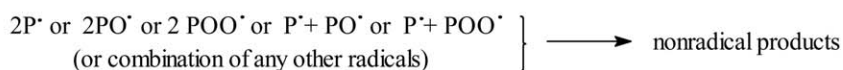
Scheme 1. The main photochemical reactions in PLA (* denotes the excited group, P·, macroradical).

strength after 5 h of photodegradation. In general, some improvement of mechanical properties is observed in the case of UV-irradiated PLA+1% Ag composites.

Discussion of Photodegradation Mechanism and Kinetics

It was reported in literature[21–24] that the main reaction in PLA subjected to UV aging is Norrish II type reaction. The

absorption of photons by carbonyl groups leads to molecule excitation (reaction 1, Scheme 1). The H atom from methyl group interacts with carbonyl oxygen and the cyclic six-membered intermediate is formed, as a result of which the chemical bond between oxygen and carbon atom (O—CH) in the main chain is weakened and finally it splits (reaction 3, Scheme 1). Consequently, the double bonds and carboxyl groups are formed at the end chains. Above reaction is nonradical and occurs owing to the presence of hydrogen atom at γ position to the carbonyl groups.

However, in our condition we can also expect the photo-oxidative degradation by free radical mechanism because the energy of 254 nm radiation is high enough to break the chemical bonds in PLA backbone. Thus, the Norrish type I reaction, that is, α-cleavage (reaction 2, Scheme 1), yielding two polymeric radicals and formation of carbon monoxide formation in subsequent process, can occur (reaction 2, Scheme 1). Moreover, the breaking of $C(CH_3)$—O bonds in main chain is also possible (reaction 4, Scheme 1). The formed macroradicals can next undergo decarboxylation. The main chain scission reactions have been proved by viscometry.

Any radicals formed in primary process can abstract hydrogen atom from polymeric chain or methyl side-group giving macroradicals of different type (reaction 5, Scheme 1). Similar macroradical products are created directly for excited PLA.

As a result of creation of free radicals in primary processes, the subsequent secondary reactions lead to numerous degradation products. In the presence of air atmosphere, the formed radicals react fastly with oxygen, and peroxy radicals ($POO^{\cdot}$) are formed (reaction 6). This reaction depends on the concentration and diffusion rate of oxygen. After that, $POO^{\cdot}$ radicals abstract hydrogen (mainly from tertiary carbon atom) generating unstable hydroperoxides (POOH). Chains containing hydroperoxide groups undergo photolysis with formation of acyl ($PO^{\cdot}$) and small hydroxyl radicals ($HO^{\cdot}$). Acyl radicals lead to formation of hydroxyl groups by H abstraction form the same or another macromolecule.

Our study confirms PLA photo-oxidation—new hydroxyl and carbonyl bands were detected in FTIR spectra. The additional carbonyl groups are formed at the end chains (CHO, COOH) or in backbone—resulting in transesterification (reaction 7), which can be intermolecular or intramolecular process. Besides hydroxyl groups, also carboxyl end groups are able to participate in this reaction. The new carbonyls exist in different circumstance, thus their absorption band is shifted in comparison to the position of C=O in spectrum of origin PLA.

As suggested in FTIR Results of UV-Irradiated PLA and PLA/Ag Nanocomposites section, perester (RCOOOR) groups can be created during combination of peroxy ($POO^{\cdot}$) and acyl ($^{\cdot}C=O$) radicals. The concentration of these moieties, similarly as end-double bonds (formed as a result of chain breaking) is very low, thus, their detection by FTIR is difficult but possible owing to difference spectra analysis. All types of radicals (alkyl, peroxyl, hydroxyl, and acyl) participate in the termination (mostly recombination) processes (reaction 8).

The nanosilver particles introduced to PLA only slightly absorb UV-irradiation. On the other hand, the polyvinylpyrrolidone (PVP) used as stabilizing agent, protecting aggregation of silver nanoparticles, is also responsible for absorption in range of 250–270 nm. Although PVP content in our composites is very low, its absorption cannot be neglected in discussion because of higher extinction coefficient at 254 nm comparing to PLA.

We found that photochemical reactions observed in PLA+Ag are retarded—they appear after much longer induction period than those in pure exposed PLA (Table I). Moreover, taking into account that the slope of curves in Figures 5(a,b) and 6 is lower for specimens containing silver, the rate of PLA/Ag photodegradation is slower than respected speed for pure PLA.

On the basis of prolonged induction period, we can conclude that Ag nanoparticles hamper PLA photodegradation, thus, partially stabilizes nanocomposites. It is confirmed by mechanical properties measurements.

Main chain scission, deduced from FTIR (Figure 6), and corresponding deterioration of mechanical properties, appear without induction period (in measured time-scale). Nevertheless, the efficiency of main chain scission in PLA+Ag is lower than that in PLA alone.

This stabilizing effect can be explained by higher absorption of incident radiation by nanoparticles (mainly by protecting layer of PVP), thus, fraction of photons absorbed by PLA macromolecules is reduced in composites.

The second main reason is that efficient radiation scattering increases with increase of silver content in sample (observed in UV-Vis spectra, Figure 1). It can be also expected that in the case of PLA+Ag, the excitation energy can be lost in intramolecular or intermolecular energy transfer or else in nonharmful physical processes such as internal conversion and vibrational relaxation. In these radiation-less processes, excited macromolecules come back to ground states without any changes in chemical structure.

It seems also possible that metallic Ag participates in photoinduced electron transfer to macromolecules, thus it can act as reduction agent ($Ag^0 \rightarrow Ag^+ + e$), which reacts with photooxidation products. The charge transfer (CT) between metal and ligand carbonyl group (so called metal-to-ligand CT) is known in UV-exposed complexes of polymers with transition metals.[25] In addition, the PVP coordination with silver occurs also via nitrogen atoms.

CONCLUSIONS

Resulting of exposure to UV, PLA and its composites with silver nanoparticles undergo random main chain scission and structural changes in different time-scale. The photochemical reactions induce also changes in molecular order and decrease the glass transition as well as melting temperature with prolonged exposure time.

The results obtained from FTIR spectroscopy and DSC analysis, supported by mechanical resistance tests, enable to establish that pure PLA and its nanocomposites with silver undergo

similar molecular changes upon UV-exposure (no differences in degradation product detected by FTIR) but photodegradation in PLA with Ag specimens starts later (after longer induction period). This hampering effect of Ag nanoparticles allows to conclude that PLA+Ag nanocomposites are characterized by improved photostability compared to unmodified PLA. The modification of PLA by nanosilver allows to obtain the environmentally friendly, biodegradable material with antibiocidal activity.

ACKNOWLEDGMENTS

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