J Polym Environ (2015) 23:316–320
DOI 10.1007/s10924-015-0720-0

ORIGINAL PAPER

Modulation of Biodegradation Rate of Poly(lactic acid) by Silver Nanoparticles

Giuliana Gorrasi[1] · Andrea Sorrentino[2] · Roberto Pantani[1]

Published online: 7 April 2015

Abstract The control of biodegradation rate is even more important than the characteristic of biodegradability itself. This is the reason why it is critical to find additives able to modulate the biodegradation rate of biodegradable polymers in relationship to the expected lifetime. This paper reports the effects of silver nanoparticles (AgNP) on the biodegradation behavior of the poly(lactic acid) (PLA). Different amounts of AgNP (0.01; 0.07; 0.12 wt%) were melt mixed with a commercial PLA in order to analyze their effect on the composites properties. The composites were submitted to biodegradation tests in controlled composting conditions, according to ASTM D 5338 and ISO14855 standards. Thermal properties of PLA and composites were analyzed at different biodegradation times. The aim was the tuning of the biodegradation rate of PLA by the addition of silver nanoparticles.

Keywords Poly(lactic acid) · Biodegradation · Composting · Silver nanoparticles

Introduction

The incorporation of antimicrobial agents into plastic products is desirable for developing value added avant-garde plastic products that prevent surface borne contamination and diseases, last longer and have better appearance. The most widely used antimicrobial additives for plastics are either organometallics, e.g. tributyl tin (TBT) and oxybisphenoxy arsine (OBPA), or small molecule organics like triclosan and octyl isothiazolinones (OIT) [1, 2]. Although these additives provide manufacturing and cost benefits, they suffer from substantial environmental and human toxicity issues. Silver based antimicrobial formulations are ideally positioned to replace existing toxic antimicrobial additives, and are finding ever increasing use in a variety of industrial, commercial, medical and institutional settings. Silver is a potent broad-spectrum antimicrobial agent with proven biocidal activity towards bacteria, fungi, virus, mold and spores [3]. The active component of silver based antimicrobials is thought to be the soluble silver ion, Ag^+, which leaches into the surrounding milieu to kill the pathogenic microbe. A number of mechanisms have been proposed for the observed biocidal effect of Ag^+ ion. Ag^+ ion is known to deactivate cellular enzymes and DNA by coordinating to electron donating groups such as thiols, carboxylates, amides, imidazoles, indoles, hydroxyls, etc. [4]. Silver is also know to cause pits in bacterial cell wall leading to increased permeability and cell death [5]. The emerging field of nanotechnology has assisted the resurgence of silver based antimicrobial formulations and products in the bioplastic field, healthcare industry and daily use products. Some composites PLA–silver nanophase have been described in literature [6–9], and have been shown to have several advantageous properties due to the nanoscopic effect e.g. enhanced release of biocidal Ag^+ ion over time due to high surface area of silver nanoparticles, cooperative antibacterial effect of polymer, improved mechanical and thermal properties of polymer–silver composites, controlling of biodegradation. Polylactide (PLA) is an environmental friendly, economical and commercially available

✉ Roberto Pantani
rpantani@unisa.it

[1] Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 84084 Fisciano, SA, Italy

[2] CNR, Institute for Polymers, Composite and Biomaterials (IPCB), Piazzale Enrico Fermi 1, 80055 Portici, NA, Italy

polymer that can be produced from renewable resources such as sugarcane, potatoes and corn [10, 11]. It is widely used in various medical applications for controlled drug delivery, medical implants and absorbable sutures [11]. It is biocompatible and biodegradable, and offers great potential as disposable packaging material. Despite the huge number of studies conducted on the development of PLA–nanoparticles composites [12], up to now, the control of the degradation process has received only limited attention [13]. Different applications require different degradation behavior. For example, in the case of materials used for short life applications, high rates of biodegradation are desirable. In contrast, packaging materials properties loss and protective barrier need to be coordinated during the storage period of the goods. To our knowledge, there have been no reports on the influence of silver based compounds on the biodegradation of PLA. This study is part of a broader effort to determine the effects of different fillers on the biodegradation behavior of the PLA. Here, different amounts of silver nanoparticles (0.01; 0.07; 0.12 wt%) were melt mixed with a commercial PLA. The resulting composites were submitted to biodegradation tests in controlled composting conditions, according to ASTM D 5338 and ISO14855 standards. PLA particles, removed at different biodegradation times, were characterized and the physical properties tested. The aim was the tuning of the rate of biodegradation by the addition of silver nanoparticles by means of a processing technique (namely melt blending) suitable for industrial applications.

Experimental

Materials

Polylactic acid, (trade name 2002D) was purchased from Natureworks LCC (Minnetonka, MN, USA). The D-LA enantiomer content is about 4 %, whereas the molecular weight distribution was determined to be equal to Mn = 115,000 and Mw = 215,000 [14, 15]. Silver nanopowders with particle size <150 nm, (CAS Number: 7440-22-4) were purchased from Sigma-Aldrich (Milan, Italy). Before any test or processing, the material was dried for 24 h under vacuum at a temperature of 60 °C.

PLA was melt mixed with different percentage of AgNP in a Brabender (DCE330) machine (screw length 400 mm, L/D = 20). The temperature of the cylinder was 200 °C, whereas the screw velocity was 40 rpm. A round die having a diameter of 4 mm and a length of 16 mm was applied. The residence time of the material inside the extruder was about 1 min. PLA is extremely sensitive to processing conditions so that a significant reduction in molecular weight takes place due to thermal and mechanical degradation [10, 16]. It is therefore clear that the biodegradation of virgin PLA can lead to results extremely different from that of the processed material. For that reason, even if the processing conditions chosen in this work minimizing the thermo-mechanical degradation [17], a direct control was carried out by analyzing both the PLA virgin material and the processed one (namely melt mixed, referred to in the following as PLA_mixed) in the same conditions utilized for the PLA/AgNP composites. The glass transition temperature (Tg) of the melt mixed PLA, as measured by DSC during a heating ramp at 10 °C/min was found to be 59.5 °C, about 0.5 °C lower than that measured on virgin PLA. This indicates a minimum degree of degradation induced by processing.

All specimens for the following biodegradation tests were prepared by milling the sample up to an average dimension of about 0.2 mm.

Methods

Biodegradation tests, conducted in controlled composting conditions (according to ASTM D 5338 and ISO14855 standards), were evaluated by a respirometric system [18]. The system is capable of measuring the metabolism of living organisms, monitoring the production of carbon dioxide by means of an infrared sensor. The compost used, coming from municipal waste, was kindly supplied from the AMA plant in Maccarese (ROME). The reactors loaded with 100 g of samples and 600 g of compost were conditioned at 58° ± 2 °C and periodically mixed and moistened during the test. The molar concentration of CO_2 was determined by the infrared analyser and elaborated according to the following equation:

$$gCO_2 = F \cdot t \cdot c \cdot P_{mco_2} \quad (1)$$

where gCO_2 is the mass of evolved CO_2; F is the gas flow rate (moles/min); t is the degradation time (min), c is CO_2 concentration measured by the analyzer (moles/moles); P_{mco_2} is the molecular weight of CO_2 (44 g/mol). The mineralization (Min) can then be estimated by the following equation:

$$Min = \frac{gCO_2 - gCO_2 b}{gCO_2 mat} \quad (2)$$

where gCO_2b is the amount of CO_2 produced by the compost and gCO_2mat is the theoretical amount of CO_2 that can be released by the sample upon total oxidation of incubated materials.

Thermal analysis (TG–DTA) was carried out in nitrogen atmosphere with a Mettler TC-10 thermobalance from room temperature to 800 °C at a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) measurements were carried out using a thermal analyzer Mettler DSC 822/400 under N_2 atmosphere. Samples were submitted to the following thermal cycles: heating at a rate of 10 °C/min from 0 to 200 °C, isothermal step at 200 °C for 5 min, cooling at a rate of 10 °C/min from 200 to 0 °C, heating at a rate of 10 °C/min from 0 to 200 °C.

Results and Discussion

Biodegradation Behavior

The benefits of silver materials incorporated into polymers have been recognized in many applications, including packaging, due to the strong antimicrobial activity of Ag against a broad spectrum of bacteria, viruses, and fungi [19]. Figure 1 reports the results of the biodegradation tests in compost, as the production of CO_2 as function of time for all samples. The values reported are averaged on three vessels for each sample. Normally, mineralization is obtained considering the difference between the amount of CO_2 produced by a vessel containing compost and sample and the amount of CO_2 produced by the compost alone. In this work, it was chosen to show the amount of CO_2 instead of mineralization because of the particular behavior of the composites samples. In fact, for higher concentrations of AgNP (0.07 and 0.12 %), the CO_2 production is lower than that of the compost alone, determining an erroneous negative value for the mineralization (Eq. 2).

It is clear from the plots that the melt mixed PLA shows a degradation rate very similar to that of the virgin PLA confirming the low effect of processing on the material. The plots corresponding to PLA with different silver concentration clearly shows that the addition of silver in PLA had a tendency of significantly decrease the degree of biodegradation. After a few days of composting, the vessel containing the samples produces less CO_2 than the compost itself. The CO_2 production starts to increase after about 30 days for composites with 0.01 and 0.07 wt% of Ag, and after more than 40 days for composite filled with 0.12 wt% of silver. The presence of silver inhibits the activity of the microorganisms and lowers the production of CO_2 at relatively short times. After some time the microbial activity starts again probably because of the development of colonies less sensitive to silver. A reduction of antimicrobial activity due to passivation could also take place. The antimicrobial action of silver nanoparticles is mainly due to the high surface area and associated to the increased potential for the release of Ag^+. An antimicrobial mechanism of silver nanoparticles was suggested. It was associated to membrane damage due to free radicals derived from the surface of the nanoparticles [20]. Silver nanoparticles may accumulate in the bacterial cytoplasmic membrane, causing a significant increase in permeability, with subsequent cell death [5].

TGA Analysis

The thermogravimetric analysis of some of the samples, taken at selected times of composting, is reported in Fig. 2. After 7 days of composting, all the samples show the typical thermogravimetric behavior of PLA: they start to loose weight at about 300 °C, at 360 °C the mass is about 50 % of the initial value, at 380 °C most of the mass has been lost. On increasing time, the curves move toward lower temperatures. The unfilled sample, after 25 days of composting, presents a behavior much different from the starting one: the weight loss starts at very low temperatures (about 50 °C) and the mass reduces continuously on

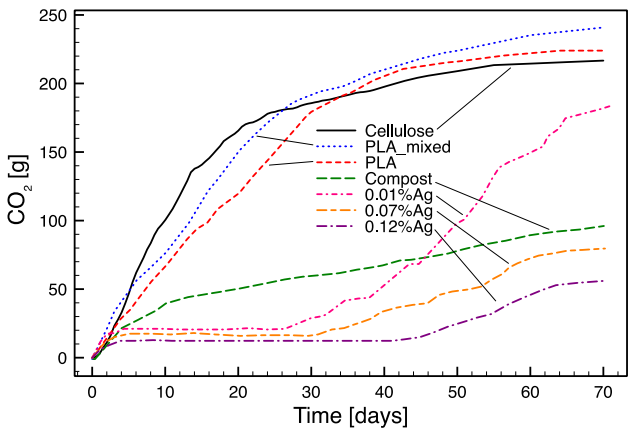

Fig. 1 Biodegradation tests in compost: production of CO_2 as function of time for PLA and composites

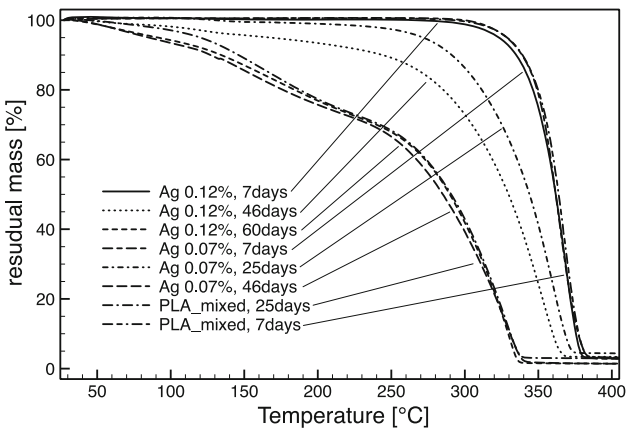

Fig. 2 TGA analysis in nitrogen atmosphere for PLA and composites at different biodegradation times

increasing temperature up to about 340 °C, temperature at which the weight reaches about 2 % of the initial value. The sample containing 0.07 % of silver nanoparticles also moves between the same two curves, but more slowly: the TG analysis after 25 days shows that weight loss starts at about 100 °C, but is confined to a few percent until about 250 °C; afterwards, the sample looses quickly weight up to about 370 °C. After 46 days, the sample with 0.07 % of silver behaves like the unfilled sample after 25 days. The sample containing 0.12 % of silver follows the same trend: after 46 days, the TGA curve lies close to the curve of the sample with 0.07 % of silver after 25 days; after 60 days, the TGA curve is very similar to those of the unfilled sample after 25 days and of the sample containing 0.07 % of silver after 46 days. Assuming that the curves at long times represent the behavior of samples with a consistent degree of mineralization, when a significant interaction has taken place between the enzymes produced by the microorganisms and the macromolecules, the data reported in Fig. 2 seem to indicate that the presence of silver nanoparticles successfully decreases the speed with which this phenomenon occurs.

Differential Thermal Analysis

The results of DSC analysis of samples at different composting time are reported in Figs. 3 and 4. The results of the first heating scan are reported in Fig. 3 to analyze the effect of composting on the samples. It is evident that the PLA samples develop a considerable crystallinity during the composting.

This effect has already been reported [18] and was attributed to the hydrolysis, which can increase the crystallization rate and to the plasticizing effect of water, which can decrease the glass transition temperature [14]. At the lowest percentages of silver, the behavior of the samples is similar to the unfilled one, but for the highest percentage of filler (0.12 %) the thermogram is different: a clear cold crystallization peak is present. The lower initial crystalline content presents in the sample would indicate that the presence of silver particles at higher concentrations can inhibit crystallization in composting conditions, possibly because of a delay of hydrolysis.

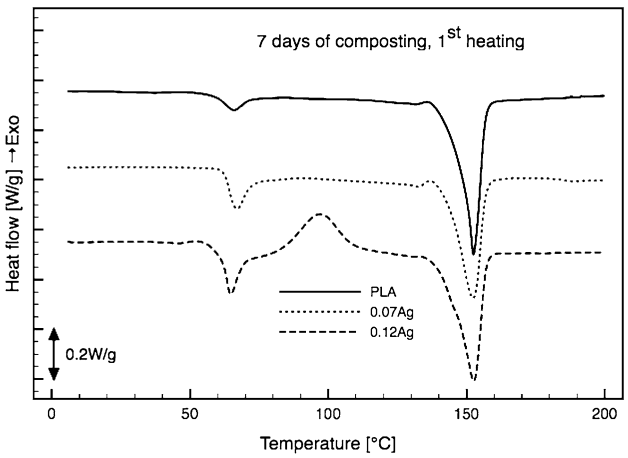

Fig. 3 Thermograms of PLA and composites with 0.07 and 0.12 wt% of Ag nanoparticles, after 7 days of composting: first heating scan

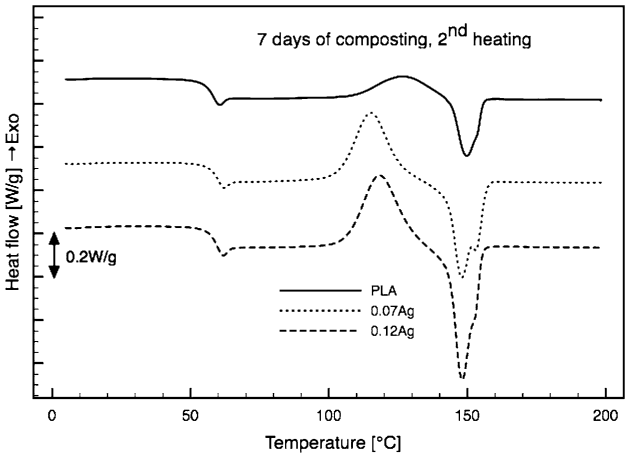

Fig. 4 Thermograms of PLA and composites with 0.07 and 0.12 wt% of Ag nanoparticles, after 7 days of composting: second heating scan

The results of the second heating scan are reported in Fig. 4 to analyze the permanent effects of composting on the material. During the second heating scan some features appear clear from the thermograms: the glass transition temperatures of the samples containing the silver particles are higher (about 60 °C instead of 58 °C) than the Tg of the unfilled sample. This indicates less degradation. The unfilled sample presents a cold crystallization peak, indicating a capacity of crystallizing in spite of the heating rate (10 °C/min) which normally does not allow to this material any crystallization [15]. The nucleating effect of silver is evident from the other thermograms, since the cold crystallization peak for the samples containing silver particles is much more evident and appears at lower temperatures.

The thermograms collected during the second heating scan on the samples after 60 days of composting are reported in Fig. 5. It can be noticed that the glass transition temperature reduced to about 40 °C, thus revealing a severe reduction of molecular weight. The unfilled sample loses any capacity of crystallizing during heating: this effect has been attributed to the interactions of the PLA with the enzymes secreted by microorganisms during degradation. In agreement with the fact that silver nanoparticles protect the material from the microorganisms, the samples containing the filler preserve the capacity of crystallizing. The crystallization and melting temperatures reduce drastically with respect to the first days of degradation because

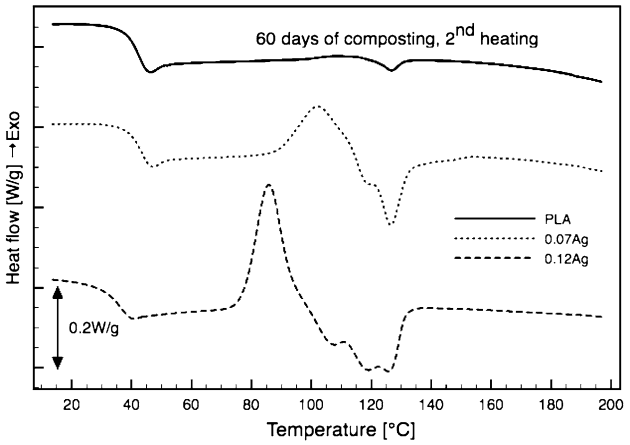

Fig. 5 Thermograms of PLA and composites with 0.07 and 0.12 wt% of Ag nanoparticles, after 60 days of composting

of the presence of smaller crystals due to the hydrolitic degradation.

Concluding Remarks

PLA and composites with different nano-silver amounts (0.01; 0.07; 0.12 wt%) were prepared by melt mixing. Samples were analyzed after different composting times. The aim was to investigate the effect of Ag nanoparticles on the reduction of biodegradation rate.

- The addition of silver in PLA significantly decreased the degree of biodegradation. The CO_2 production starts to increase after about 30 days for composites with 0.01 and 0.07 wt% of Ag, and after more than 40 days for composite filled with 0.12 wt% of silver
- The thermogravimetric analysis seems to indicate that the presence of silver nanoparticles successfully decreases the speed with which the interaction between the enzymes produced by the microorganisms and the macromolecules takes place
- This is also confirmed by DSC analysis: after 60 days of composting, the unfilled sample loses any capacity of crystallizing during heating whereas the samples containing the filler preserve the capacity of crystallizing.

The efficiency of antimicrobial function of the polymeric nanocomposites is greatly influenced by several factors such as silver content, particle size, size distribution, degree of particle agglomeration, interaction of silver surface with the base polymer. Work is in progress to investigate the effect of Ag particle size on the biodegradation behavior of PLA.

References

1. D'Arcy N (2001) Antimicrobials in plastics: a global review. Plast Addit Compd 3:12–15
2. Holley S, Gastrock F, Ice ML (2002) Antimicrobial plastics additives: trends and latest developments in North America. Plast Addit Compd 4:18–21
3. Russell AD, Hugo WB (1994) 7 Antimicrobial activity and action of silver. In: Ellis GP, Luscombe DK (eds) Progress in medicinal chemistry. Elsevier, Amsterdam, pp 351–370
4. Holt KB, Bard AJ (2005) Interaction of silver(I) ions with the respiratory chain of *Escherichia coli*: an electrochemical and scanning electrochemical microscopy study of the antimicrobial mechanism of micromolar Ag^+. Biochemistry 44:13214–13223
5. Sondi I, Salopek-Sondi B (2004) Silver nanoparticles as antimicrobial agent: a case study on *E. coli* as a model for Gram-negative bacteria. J Colloid Interface Sci 275:177–182
6. Pillai SK, Ray SS, Scriba M, Ojijo V, Hato MJ (2013) Morphological and thermal properties of photodegradable biocomposite films. J Appl Polym Sci 129:362–370
7. Fortunati E, Armentano I, Iannoni A, Kenny JM (2010) Development and thermal behaviour of ternary PLA matrix composites. Polym Degrad Stab 95:2200–2206
8. Shameli K, Ahmad MB, W Md Zin Wan Yunus, Ibrahim NA, Rahman RA, Jokar M, Darroudi M (2010) Silver/poly (lactic acid) nanocomposites: preparation, characterization, and antibacterial activity. Int J Nanomed 5:573–579
9. Xu X, Yang Q, Wang Y, Yu H, Chen X, Jing X (2006) Biodegradable electrospun poly(l-lactide) fibers containing antibacterial silver nanoparticles. Eur Polym J 42:2081–2087
10. Garlotta D (2001) A literature review of poly(lactic acid). J Polym Environ 9:63–84
11. Rasal R, Janorkar A, Hirt D (2010) Poly(lactic acid) modifications. Prog Polym Sci 35:338–356
12. Bordes P, Averous L (2009) Nano-biocomposites: biodegradable polyester/nanoclay systems. Prog Polym Sci 34:125–155
13. Stloukal P, Kalendova A, Mattausch H, Laske S, Holzer C, Koutny M (2015) The influence of a hydrolysis-inhibiting additive on the degradation and biodegradation of PLA and its nanocomposites. Polym Test 41:124–132
14. Gorrasi G, Pantani R (2013) Effect of polylactic acid grades and morphologies on hydrolytic degradation at composting temperature: assessment of structural modification and kinetic parameters. Polym Degrad Stab 98:1006–1014
15. Pantani R, De Santis F, Sorrentino A, De Maio F, Titomanlio G (2010) Crystallization kinetics of virgin and processed poly(lactic acid). Polym Degrad Stab 95:1148–1159
16. Pillin I, Montrelay N, Bourmaud A, Grohens Y (2008) Effect of thermo-mechanical cycles on the physico-chemical properties of poly(lactic acid). Polym Degrad Stab 93:321–328
17. Speranza V, De Meo A, Pantani R (2014) Thermal and hydrolytic degradation kinetics of PLA in the molten state. Polym Degrad Stab 100:37–41
18. Pantani R, Sorrentino A (2013) Influence of crystallinity on the biodegradation rate of injection-moulded poly(lactic acid) samples in controlled composting conditions. Polym Degrad Stab 98:1089–1096
19. Russell AD, Hugo WB (1994) 7 Antimicrobial activity and action of silver. In: Progress in medicinal chemistry, pp 351–370
20. Kim JS, Kuk E, Yu KN, Kim JH, Park SJ, Lee HJ, Kim SH, Park YK, Park YH, Hwang CY, Kim YK, Lee YS, Jeong DH, Cho MH (2007) Antimicrobial effects of silver nanoparticles. Nanomed Nanotechnol Biol Med 3:95–101