Biodegradation of a Polylactic Acid/Polyvinyl Chloride Blend in Soil

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Received 16 September 2010; accepted 20 September 2011
DOI 10.1002/app.35685
Published online 22 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: This study investigated the microbial action in soil on poly(L-lactic acid) (PLLA) and polyvinyl chloride (PVC) films and a PLLA/PVC 7 : 3 blend, using Fourier transform infrared spectroscopy (FTIR), contact angle and scanning electron microscopy (SEM). The films (50 μm) were obtained from the evaporation of dichloromethane solutions and buried in soil columns, in controlled conditions, for 120 days. The results showed that the surface of the PLLA films and blend became 18 and 31% more hydrophilic, respectively. The morphology of the films also changed after 120 days of microbial treatment, particularly that of the PLLA phase in the blend, confirmed by structural and conformational changes in the FTIR CO region at 1200–1000 cm^{-1} and an increase in the relative intensity of the band at 1773 cm^{-1}, which was attributed to C=O group vibration due to a rotational isomer in the interlamellar region (semi-ordered region). Besides the biotreated PVC presented changes in the C—Cl band at 738 cm^{-1}, due to the presence of some PVC conformational isomer. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 536–540, 2012

Key words: PLLA; PVC; FTIR; biodeterioration; contact angle

INTRODUCTION

More than half a century ago, synthetic polymers began to replace natural materials in almost every area, and now plastics have become an indispensable part of our lives. Durable and stable, they have been continuously improved and are considered to be a material resistant to environmental influences.[1] The ever increasing consumption and disposal of these materials worldwide has been a key concern for society and the scientific community. Plastic waste is recognized as one of the most problematic categories of waste.[2] Synthetic polymers are resistant to microbial attack mainly because they have not been in existence long enough for polymer-degrading enzymes to develop naturally.

Polyvinyl chloride (PVC) is a synthetic, amorphous, non-biodegradable polymer with high T_g (80–85°C) that is widely used in packaging, flooring, roofing, hoses, curtains, and toys.[3,4] It has been mixed with many other polymers to improve their mechanical properties and widen their range of applications in trade and industry.[5] Despite the instability of PVC when exposed to light, its waste persists in the environment.[6]

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Journal of Applied Polymer Science, Vol. 125, 536–540 (2012)

Several types of aliphatic polyesters such as polyhydroxyalkanoates (PHAs), poly(ε-caprolactone) (PCL), and poly(L-lactic acid) (PLLA) have been developed as green, biologically recyclable polymers.[7] Three categories of biodegradable polymers can be distinguished: (1) biopolymers produced by plants, animals, and microorganisms, such as cellulose, starch, chitin, and polyhydroxyalkanoates (PHAs), (2) synthetic polymers such as polylactic acid (PLA), poly(ε-caprolactone) (PCL), poly(ethylene/butylene succinate), and poly(ethylene/butylene adipate), and (3) polymer blends suitable for natural and synthetic systems such as starch/PCL. Some are commercially available as products – Biopol, Eco-PLA and Bionolle.[8]

Poly(L-lactic acid) (PLLA) is a biodegradable polymer with a glass transition temperature (T_g) of 60°C and melting point temperature (T_m) of around 130–180°C,[9] which is used in medical implant products and controlled-release capsules of drugs.[10] It is an important polymer due to its technical properties, good biocompatibility and biodegradability, and mechanical properties.[11] Due to the presence of ester groups in the chain, it can be hydrolyzed in the human body.[12] The difficulties encountered in processing PLLA have remained the major limiting factor in applications.[13,14]

The development of blends susceptible to microbial attack is of great importance to relieve the environment of a significant amount of plastic waste.[15] Blends of PLLA with biodegradable polymers have

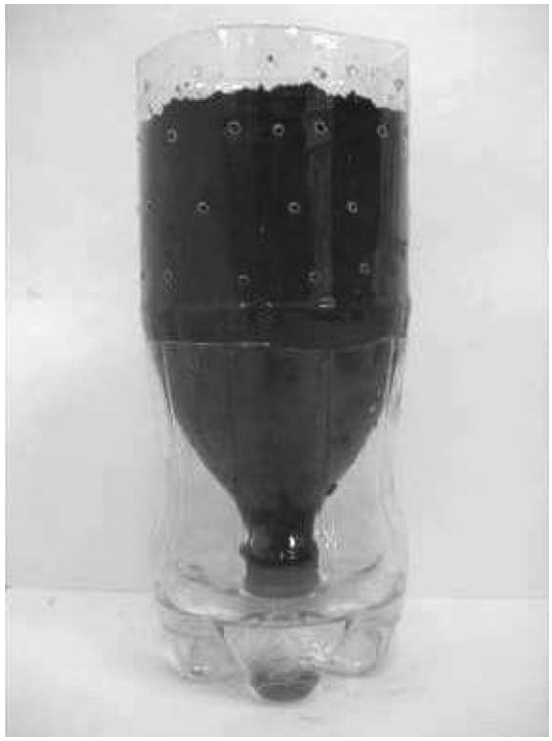

Figure 1 Soil column used for the biotreatment.

been used as medical materials due to their biodegradability and biocompatibility. These polymers are polyvinyl alcohol (PVA), poly(ε-caprolactone) (PCL), polyhydroxybutyrate (PHB), polyethylene oxide (PEO), and poly(D-lactic acid) (PDLA).[16] However, biodegradation is undesirable in some cases such as in consumer electronics and some automotive parts, which require good mechanical properties. Indeed, the ideal would be for PLLA to be stable during use and rapidly degradable after it is discarded; therefore, controllable degradation is a very important requirement.[16] To improve its technological processing and availability to the enzymatic hydrolysis Arvanitoyannis et al.[17] used glycerol in the synthesis of PLLA. Lovera et al. 2007[18] showed that unlike homopolymers, PHB/PCL blends are attacked synergistically, due the dispersion of the components, but the increased miscibility between the components causes reduction in the degradation rate. The biodegradation of PHB appears to trigger morphological changes in PCL as well in the immiscible blend of PP/PHBV.[19] Biodegradation is one of the ways to reduce the waste amount of polymers in the environment. Another ways can be landfill, incineration, pyrolysis, re-use and recovery, composting, and recycling.[20]

This work investigated the biodegradation of a PLLA/PVC blend and homopolymers through the action of soil microorganisms, using Fourier transform infrared spectroscopy (FTIR), contact angle, optical microscopy, and scanning electron microscopy (SEM).

MATERIALS AND METHODS

Preparation of films

Films were prepared using PLLA (M_w: 100,000 g/mol), PVC (M_w: 73,491 g/mol – Sigma-P-9401), and the PLLA/PVC 7 : 3 blend. All the homopolymer films and the blend (in duplicate) were obtained from diluted solutions of dichloromethane (CH_2Cl_2, p.a) to 8 g/L. The solutions were magnetically stirred at 50°C for 30 min. They were then placed in Petri dishes (5 cm in diameter), in a vacuum oven (100 mmHg) at a controlled temperature (27°C) to evaporate the solvent, slowly to obtain uniform films and keeping the same thickness (approximately 50 μm). After the solvent was dry, the films were put in a vacuum desiccator and left there for 48 h.[21] Each film (in duplicate) was cut into two parts. One of them was kept as control sample and is referred as untreated film and analyzed by FTIR, contact angle, and SEM. The other part of the same film was biotreated and then analyzed.

Preparation of soil columns

Microbial treatment took place in soil columns, prepared in plastic bottles of PET with evenly distributed holes to assist oxygenation and microbial activity. The soil was taken from the UNESP/Rio Claro campus garden and sifted through a 2 mm mesh sieve. The column was set up with 22 cm of soil and the films were buried about 10 cm below the surface. Humidity was maintained by capillary action through the holes at the bottom of the bottle, and the water was replenished weekly. Figure 1 illustrates the above described column. The biodegradation of each type of polymer film (in duplicate) was analyzed for a period of up to four months, because this time is enough to begin the biodeterioration process on polymer films, similar to the other works.[19,22]

Analytical methods

FTIR

The untreated and biotreated films were analyzed using a Shimadzu 8300 FTIR spectrometer in the range of 4000–500 cm^{-1}, with 4 cm^{-1} resolution and 16 scans. The FTIR spectra were analyzed based on the ratio of the band intensity and an internal standard band of the PLLA film, in this case at 1454 cm^{-1} (CH_2 deformation).[23] Furthermore, deconvolution curves (Lorentzian mode) were drawn to confirm the band's maxima.

Contact angle

Measurements of the contact angle of the films (in duplicate) were made by depositing a drop (about

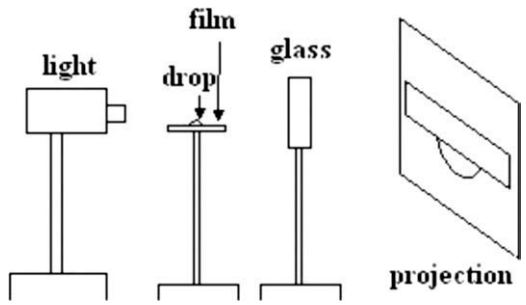

Figure 2 Schematic diagram of the experimental setup for measuring the contact angle.

10 μL) onto the surface of each film on a horizontal plane, as illustrated in Figure 2.

To calculate the contact angle, a drop of water was considered as being roughly spherical. The ratios between the angles in a circle and measurements l and h, as shown in Figure 3, were used to obtain the radius ($R = \frac{h}{1+\cos(2\beta)}$) and thus the expression of the tangent line to the drop at the point of contact with the surface. From this measurement, we derived the expression for the contact angle $\gamma = \arctan\frac{l/2}{\sqrt{R^2-(l/2)^2}}$.[24,25]

This ratio was fed into a program to automate measurements and calculate their mean value and deviation by five measurements in each sample.

Scanning electron microscopy—SEM

The electron micrographs of untreated and biotreated PLLA and PVC films, and the PLLA/PVC 7 : 3 blend, were obtained in a scanning electron microscope (SEM) Zeiss DSM 940-A, the 5KV (ESALQ-USP, Piracicaba), with 500× magnification. Each film was mounted on an aluminum support and sputter-coated with gold in a vacuum chamber, using a Balzers MED 010 mini deposition system.

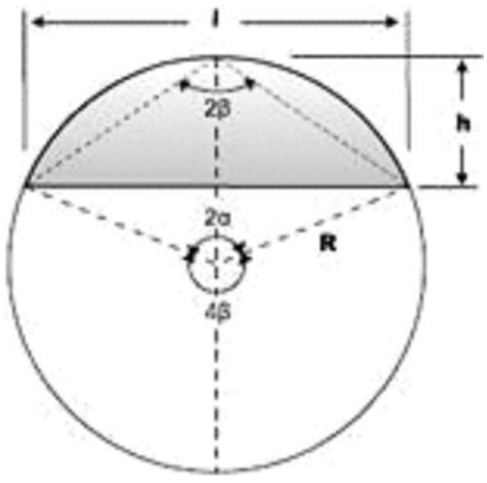

Figure 3 Approximation of a spherical drop for the contact angle calculation.

RESULTS

The films were clear with a thickness of 50 μm. Figure 4 shows the FTIR spectra of the homopolymers and the PLLA/PVC blend before and after 120 days of

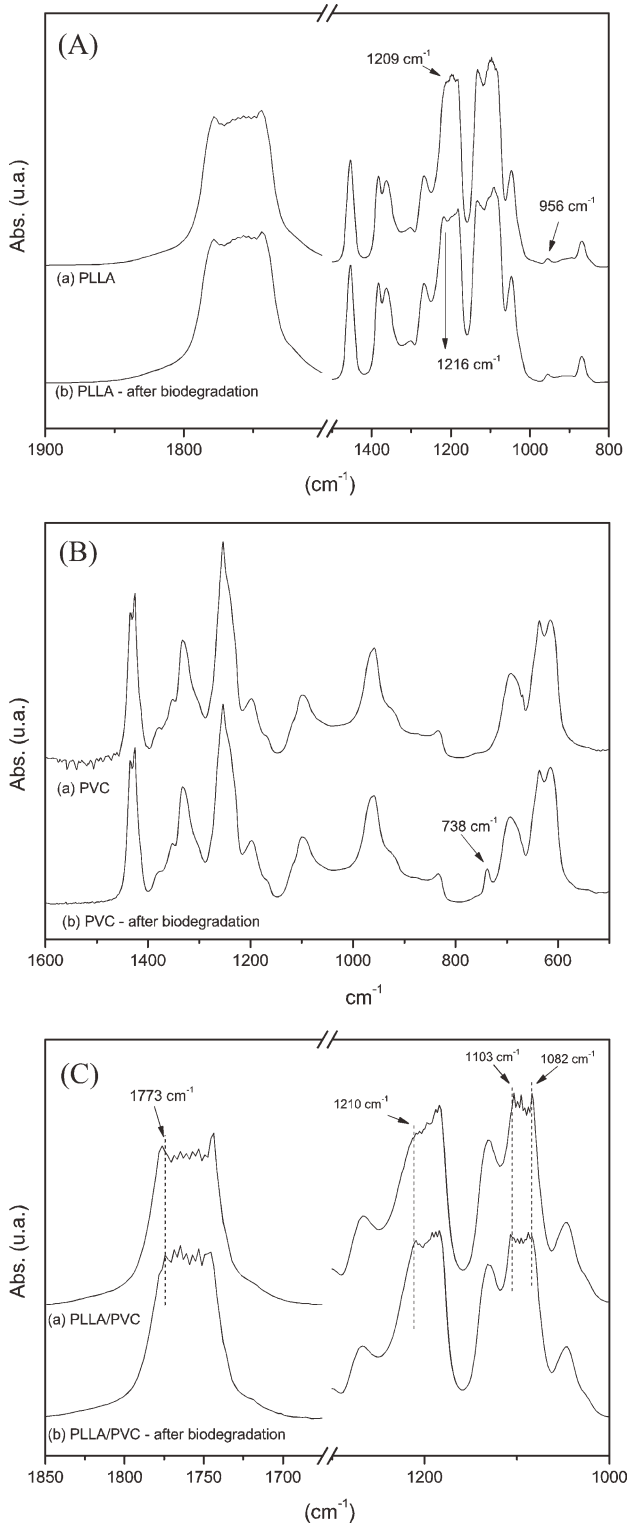

Figure 4 FTIR spectra of the biodegradation of the films in the soil column for 120 days: (A) PLLA, (B) PVC, (C) PLLA/PVC 7 : 3, respectively: a) untreated b) after biodegradation.

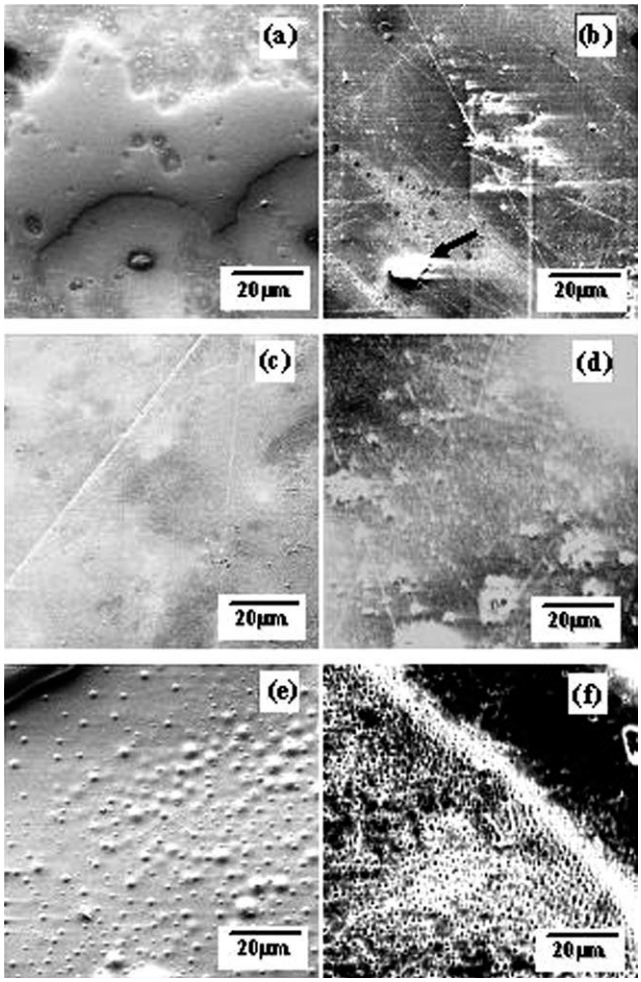

Figure 5 SEM micrographs of the biodegradation of the films in the soil column for 120 days: (a) untreated PLLA, (b) PLLA after biodegradation, (c) untreated PVC, (d) PVC after biodegradation, (e) untreated PLLA/PVC 7 : 3, (f) PLLA/PVC 7 : 3 after biodegradation.

biotreatment. These spectra were normalized in relation to the internal standard band at 1454 cm^{-1} (CH_2 deformation), which was chosen because it does not change during biodegradation. Furthermore, deconvolution curves (Lorentzian mode) were drawn to confirm the band's maxima.

After 120 days of biotreatment, the PLLA film presented a shift in the band from 1209 to 1216 cm^{-1}, which was attributed to C—O—C vibration in the crystalline phase. Meaurio et al.[26,27] reported that samples of amorphous and crystalline PLLA showed chain conformational changes, which were revealed by FTIR. Carbonyl groups in PLAs present conformational sensitivity, which can be affected by specific interactions (hydrogen bands C—H···O and dipole–dipole interactions between C=O groups) and also by their morphology.

We should also consider unfolded vibrations resulting from the association of transition dipole coupling (TDC) produced structurally.[27] This type of structure induces symmetric vibrations (a) and antisymmetric vibrations of carbonyl groups in FTIR.[18] The oxygen atom bound to the C=O and C—C groups is a good transmitter of vibrational association, as reported by Kleinpeter et al.[28] and Meaurio et al.[26] This behavior is observed in the FTIR CO region with unfolded vibrations at 1200–1000 cm^{-1}. The above-mentioned TDC may be responsible for shifts or changes in the bandwidth.[26]

The appearance of a new band at 738 cm^{-1} [see Fig. 4(b)] was attributed to C—Cl stretching due to the presence of different conformational isomers in PVC. The polymer matrix changed in response to biotreatment and morphology changes, which was reflected by conformational changes in the PVC chains.

The FTIR absorption spectra of the PLLA/PVC 7 : 3 blend films before and after biotreatment [Fig. 4(c)] showed an increase in the relative intensity of the band at 1773 cm^{-1}, which was attributed to C=O group vibration. This is due to a rotational isomer in the interlamellar region (semi-ordered region); 1210 cm^{-1} (C—CO—O) asymmetric stretching, and a decrease in the relative intensity of the band at 1103 cm^{-1} (angular deformation of C—H).

Blends of PLLA/PMMA (poly(methyl methacrylate) were prepared by both solution/precipitation and solution-casting, showed the crystallization of PLLA was greatly restricted by amorphous PMMA, and the crystallization tendency of PLLA acts as the driving force for phase separation.[29]

Rudnik and Briassoulis[23] showed that the degradation of PLA in soil is slow and that it takes a long time for the material disintegration to start. In this work, the FTIR analysis showed only the intensity of absorbance at 1748 cm^{-1} (C=O) decreased after 11 months of soil burial. The results showed that degradation in soil is a complex phenomenon, following different patterns regarding morphological changes.

The SEM micrographs (Fig. 5) revealed major morphological changes in the homopolymer films and PLLA/PVC 7 : 3 blend resulting from microbial attack on polymer surfaces. The films showed different structures in relief and traces of rupture [Fig. 5(b,f)]. These films deteriorated more than the PVC, which showed no significant changes [Fig. 5(d)]. Before the biotreatment, the PLLA/PVC blend contained some bubbles [Fig. 5(e)] as did the homopolymer films [Fig. 5(a,c)]. After 120 days buried in soil, the morphology had changed significantly [Fig. 5(f)]. This alteration, associated with conformational changes in the PLLA phase (as shown by FTIR), suggests that microbial action occurred preferentially on the PLLA surface, that is understandable because PLLA absorbs water and collapses the polymer block,

TABLE I
Contact Angle Measurements of the Films Before and After Biodegradation in the Soil Column

Sample	Contact angle (°)	Deviation (°)
PLLA – untreated	71.5	1.6
PLLA – biotreated for 120 days	58.7	1.7
PVC – untreated	74.7	1.5
PVC – biotreated for 120 days	67.1	1.7
PLLA/PVC 7:3 – untreated	75.1	2.8
PLLA/PVC 7:3 – biotreated for 120 days	51.4	2.4

which becomes available for attack by microorganisms and enzymes.[30,31]

Table I shows the contact angle results of the films measured before and after treatment in the soil column. After treatment, the three films, PLLA, PVC, and PLLA/PVC 7 : 3, showed increased hydrophilicity, respectively 18, 10, and 31%. This helps the action of microorganisms on films. However, some factors, such as the size of the water drop and sample heterogeneity, influence the measurements. In the case of the blend, whose film is highly heterogeneous, it is difficult to measure the diameter of the water drop, regardless the mean deviation giving a good reliability.

CONCLUSIONS

The PLLA and PVC films and the PLLA/PVC 7 : 3 blend underwent morphological and structural alterations after burial in soil for 120 days. The PLLA films and blend became 18 and 31% more hydrophilic, respectively. In the blend, PLLA chains presented conformational changes (FTIR) in the CO region at 1200–1000 cm^{-1} and an increase in the relative intensity of the band at 1773 cm^{-1}, which was attributed to C═O group vibration due to a rotational isomer in the interlamellar region (semi-ordered region). PVC showed conformational isomer presence in the C─Cl band at 738 cm^{-1}.

However, the morphological and molecular changes in the PLLA/PVC 7 : 3 blend were more severe than in the homopolymers. In this case, the different phases in the blend influenced microbial attack, changing the morphology and leading to conformational changes in the PLLA chains.

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