Biodegradability Assessment of Aliphatic Polyesters-Based Blends Using Standard Methods

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ABSTRACT: Important information concerning polymer's final fate in the environment can be achieved in biodegradation studies. In this context, the focus of this study was to evaluate the biodegradability of blends containing aliphatic polyesters using standard methods. Blends of high-density polyethylene, biodegradable polymer, and polyethylene modified with maleic anhydride (used as compatibilizer) were prepared in a corotating twin-screw extruder. Biodegradable polymers used were poly(lactic acid) (PLA), poly(ε-caprolactone) (PCL), and Mater-Bi (thermoplastic starch with PLA or PCL). Biodegradation tests were carried out using two standard methods: (i) ISO 14851 (1999), biochemical oxygen demand in a closed respirometer and (ii) ASTM G 22-76, microbial growth of test microorganisms. Both biodegradability tests suggested that the blend containing PCL is more biodegradable than the one containing PLA. Addition of starch increased the biodegradability of the PLA blend. The biodegradability of the blends evaluated in this study by the biochemical oxygen demand method ranged from 22% (PLA 60) to 52% for corn starch/PCL 30/70 (% wt) (SPCL 70). Therefore, the blends may not be considered "readily biodegradable" according to the OECD standard. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3338–3346, 2011

Key words: biodegradability; polymer blends; standard methods; biodegradable polymers

INTRODUCTION

The demand of synthetic polymeric materials has been fairly increasing during the last decades, and presently they are one of the most attractive categories of materials. This success is mainly related to their properties namely, low cost, esthetic qualities, resistance to physical ageing and biological attack.[1] Polyolefins are the synthetic polymeric materials with the highest commercial success, accounting for more than 47% of Western Europe's total consumption, 24.1 million tonnes per year. Polyolefins present a combination of physical properties (e.g., flexibility, strength, lightness, stability, impermeability, and easiness of sterilization) that are ideally suited to a wide variety of applications, such as, agricultural film, food and drinks packaging.[2] However, these polymers have poor oxygen barrier properties and a well-known resistance to degradation.[3,4] The growing environmental awareness and the new environmental regulations are forcing the industries to seek for more ecologically friendly materials for their products, namely in applications where they are used for a short period of time before becoming waste.

Biodegradable polymers are derived from renewable (corn or wood cellulose) or petroleum sources. The best known petroleum source-derived biodegradable polymers are aliphatic polyesters or aliphatic-aromatic copolyesters.[5] As an example, poly(ε-caprolactone) (PCL), generally prepared from the ring-opening polimerization of ε-caprolactone is a flexible aliphatic semicrystalline polyester, and it has been found to be miscible with many other polymers.[6,7] Also, PCL is appreciated by its biodegradable properties because it can be biodegraded aerobically by a large number of microorganisms in various microbiological environments.[7] However, the high cost and low performance of PCL has prevented its widespread industrial use.[8]

At present, biodegradable polymers derived from renewable sources like polylactides (PLA) compete with petroleum-based biodegradable polymers.[9] The production of PLA presents advantages over other synthetic materials: (i) PLA can be obtained from renewable agricultural sources (e.g., corn), (ii) its production consumes carbon dioxide, providing significant energy savings, and (iii) PLA is recyclable and compostable.[10–12] Early economic studies have shown that PLA is an economically feasible material

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to be used as a packaging material.[13] Medical studies have shown that the level of acid lactic (LA) that migrates to food from packaging containers is much lower than the amount of LA used in common food.[14] The properties of PLA are determined both by the polymer architecture (stereochemical make up of the backbone) and the molecular weight, being the latter controlled by the addition of hydroxylic compounds. The ability to control the polymer's stereochemical architecture allows precise control over the speed of crystallization and the degree of crystallinity, the mechanical properties, and the processing temperature of the material.[14] PLA is a polyester with one of the highest melting temperatures, around 160–180°C, thus is less susceptible to biodegradation. PLA biodegradation also depends on its crystallinity, molecular weight, shape, and morphology.[15]

Blends of biodegradable and nonbiodegradable polymers have low production costs and better mechanical properties than pure biodegradable polymers. As an example, polyolefin-starch blends commonly used in the packaging industry[16] have better mechanical properties compared to starch, and enhanced biodegradability in relation to pure polyolefin's.

Important information concerning polymer's final fate in the environment can be achieved in biodegradation studies performed in the aquatic environment. Environmental biodegradation concerns the complete conversion of organic chemicals to inorganic products mediated by microbial processes. Standard test methods have been proposed by several international organizations to assess biodegradability of polymeric materials (ASTM, ISO, OECD).[17] All of these tests simulate natural conditions. Polymers biodegradation can be measured according to the carbon dioxide mass and/or methane evolved, oxygen consumption, degradation products released (e.g., monomers), and polymer carbon converted into biomass.[17–19] Literature studies report that two main steps are involved in the biodegradation of polyesters. First, embrittlement of the polymer occurs due to random nonenzimatic chain scission of the ester groups in the polymer backbone leading to a reduction in polymer's molecular weight.[10,14] Secondly, low molecular weight oligomers diffuse out of the bulk polymer and are used by microorganisms yielding degradation products.[14] The biodegradation rate of polymers can be affected not only by the degradability of the blend components themselves but also by several parameters, such as molecular weight, phase structure (miscibility and crystallinity), surface blend composition, molecular structure, the length of the polymer chain, and melting temperature.[20–22] In general, a polymer having a lower melting temperature is more susceptible to biodegradation than one having a higher one because the polymeric chain is more flexible and can fit more easily into the active sites of enzymes.[20] Factors related to surface conditions can also affect the biodegradability, as surface area, hydrophilic and hydrophobic properties.[23]

The purpose of this study was to evaluate the aerobic biodegradability of aliphatic polyesters based blends using standard methods. Many studies on PCL and PLA in solid state have exhibited significant biodegradation within several days in water with activated sludge,[18] nevertheless there has not been done any study that compares biodegradability by two different methods. This study investigates and compares the biodegradability of high-density polyethylene (HDPE) blended with biodegradable polymers, polylactic acid (PLA), poly (ε-caprolactone) (PCL), and Mater-Bi (thermoplastic starch with PLA or PCL) under different testing methods of existing standards. Thus, our research focuses on the addition of biodegradable polymers to HDPE, as a blend with improved mechanical properties maintaining their biodegradability.[5]

MATERIALS AND METHODS

Materials

Materials used in this study are commercially available. HDPE, 2008SN60, was provided by Total, polyethylene modified with 3.1% (wt) maleic anhydride (PE-g-MA), Lotader 3210, was supplied by Arkema, PCL, CAPA FB100, was supplied by Solvay, and PLA, Polymer 2002D NatureWorks®, was obtained from Novamont. Starch-based thermoplastics (TPS), Mater-Bi®, were supplied by Novamont. Mater-Bi® are commercially available as blends of corn starch/PCL 30/70 (% wt), SPCL 70, corn starch/PLA 30/70 (% wt), SPLA 70, and corn starch/PLA 50/50 (% wt), SPLA 50.

Blends preparation

To compound the blends used in this study (Table I), materials were tumble mixed and processed in a laboratory modular corotating twin screw extruder (Leistritz LSM 30.34) using a barrel temperature of 190°C, a screw speed of 100 rpm, and a throughput of 3 kg/h. The extruded material was air cooled, dried, and cut in small pellets.

Biodegradation tests

The aerobic biodegradation of the blends prepared in this study was investigated using two distinct methods: microbial growth in polymeric films and biochemical oxygen demand.

TABLE I
Composition of the Blends Expressed as Weight Percentages

Blend	HDPE	PE-g-MA	PLA	PCL	Mater-Bi
PLA 60	30	10	60	0	0
PCL 60	30	10	0	60	0
SPLA 50	30	10	0	0	60 (50 TPS + 50 PLA)
SPLA 70	30	10	0	0	60 (30 TPS + 70 PLA)
SPCL 70	30	10	0	0	60 (30 TPS + 70 PCL)

Microbial growth test

The growth of a pure culture of Pseudomonas fluorescens was evaluated as a function of time with HDPE and the polymeric blends previously described (Table I) as sole carbon and energy sources. The experimental procedure was adapted from ASTM G 22-76 (the essays were carried out in liquid phase instead of solid phase).[24] Each sample, shaped as a disc with 25 mm diameter and thickness of 0.25 mm, was decontaminated with ethanol 70% (v/v) and placed into sterilized conical shaped 100 mL Erlenmeyer flasks containing 40 mL of R2A carbon-free medium at pH 7.0. Each flask contained one disk divided into two halves and the disk's density was lower than the water density. The flasks were closed with stoppers connected to air filters and spiked with the pure culture directly from an agar plate and incubated under static conditions at room temperature (22°C). Bacterial density on the surface of the polymer, forming a biofilm, was monitored by total cell counts over a period of 10 weeks. Cells were enumerated by epifluorescence microscopy after DAPI staining (5 min, 2 mg/L final concentration) at 1000 magnification. The detailed methodology is described in Machado et al.[5]

Biochemical oxygen demand test

Biodegradation tests were carried out in aqueous environment under aerobic conditions according to the standard ISO 14851:1999 (Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium)[25] which specify a method for determining the biochemical oxygen demand (BOD) in a closed respirometer. Polymers were reduced to powder to create a suspension of the polymer in the test system. The Oxitop system used in the determination of BOD contains an individual number of reactors consisting of glass bottles with a carbon dioxide trap (sodium hydroxide) in the headspace. The bottles are supplied with a magnetic stirrer and sealed with a cap containing an electronic pressure indicator. BOD determinations were carried out in 510 mL bottles containing 62.5 mg of the test blend, 2 mL of inoculum, and 50 mL of mineral medium. The mineral medium contained 40 mL/L of solution A (28.25 g/L KH_2PO_4, 146.08 g/L K_2HPO_4), 30 mL/L of solution B (3.36 g/L $CaCl_2{\cdot}2H_2O$, 28.64 g/L NH_4Cl), and 30 mL/L of solution C (3.06 g/L $MgSO_4 \cdot 7H_2O$, 0.7 g/L $FeSO_4 \cdot 7H_2O$, 0.4 g/L $ZnSO_4$). The source of inoculum was activated sludge freshly sampled from a municipal sewage treatment plant. The BOD of the inoculum was determined in blank tests performed only with mineral medium and inoculum. These values were subtracted from the BOD values of the blends to obtain exact values of the degradation activity. Test bottles were incubated at 30°C in the dark with stirring for more than 28 days. The experiments were carried out with and without nitrification inhibitor, allylthiourea (ATU), at a concentration of 10 mg/L, in triplicate. The amount of O_2 consumed in polymer's biodegradation (after correction with the blank test) was expressed as a percentage of the theoretical oxygen demand (ThOD). The ThOD expressed as mass of O_2 per mass of polymer was determined by calculating the amount of O_2 necessary for aerobic mineralization of the polymer, i.e., complete oxidation of C to CO_2.[26] The ThOD of the polymer $n(C_cH_hO_o)$, with a relative molecular mass M_r (per monomer), was calculated according to:

$$\mathrm{ThOD} = (31.9988/M_r)(\mathrm{c} + 0.25\mathrm{h} - 0.5\ \mathrm{o})$$

Characterization methods

The composition of all samples was determined by elementary analysis on a LECO CHNS-932. The samples' chemical formulas are the following: PLA 60, C_3H_5O; PCL 60, $C_5H_{10}O$; SPLA 50, C_5H_9O; SPLA 70, C_3H_4O; SPCL 70, C_3H_7O.

The biodegradation of the polymers and blends was followed by FTIR spectroscopy (Perkin–Elmer 1720 spectrometer). Measurements were recorded in a transmittance mode in the range of 4400–400 cm^{-1}, using 16 scans with a resolution of 4 cm^{-1}. Thin films of the initial materials and the residues after biodegradation were prepared by compression-molding and analyzed directly using a solid film support.

RESULTS AND DISCUSSION

Biodeterioration of polymer films by the microbial growth method

Blends were incubated in the presence of *Pseudomonas fluorescens* under defined experimental conditions

TABLE II
Ratio Between the Biofilm Bacteria Number on Polymeric Samples Quantified in the 10th Week and in the 2nd Week of Experiment Lifetime (Values Listed in the Table Are the Average ± 95% Confidence Interval)

HDPE	PLA 60	PCL 60	SPLA 50	SPLA 70	SPCL 70
1.75 ± 0.14	2.71 ± 0.31	3.49 ± 0.80	4.59 ± 1.21	2.98 ± 0.83	3.29 ± 0.27

according to the standard ASTM G 22-76 which specifies a method for determining the microbial growth of a test microorganism. An increase of bacterial ratio along time was observed in the biofilm formed on the surfaces of all blends (Table II). HDPE, used as a negative control, showed the lowest cell count ratio while SPLA 50 exhibited the highest. There could be two main factors that contributed to the experimental results obtained: on the one hand, HDPE has a lower surface energy being a less favorable material to cell adhesion[27]; on the other hand, resistance to microbial attack is lower for SPLA 50 because of the presence of starch and PLA.[28] The cell count ratio of PCL 60 was higher than the one of PLA 60, as depicted in Table II, suggesting that PCL is less resistant to bacterial attack than PLA. This result might be explained based on chemical structure.[29] Because of the stereochemical structure of PLA, it can promote sterique hindrance and make the hydrolysis more difficult. Another parameter that become PLA less susceptible to biodegradation than PCL, has been related with melting temperature.[15] Polymers with low melting temperature are more susceptible to biodegradation because the polymeric chains are more flexible and the enzymes active sites can fit easily into them. Since PCL has lower melting temperature than PLA, it would facilitate the microorganism attack resulting in higher biodegradation. The blends morphology could also explain this difference.[5] While PLA 60 exhibits a coarse morphology, PCL 60 has smaller particles and low interfacial tension with HDPE.

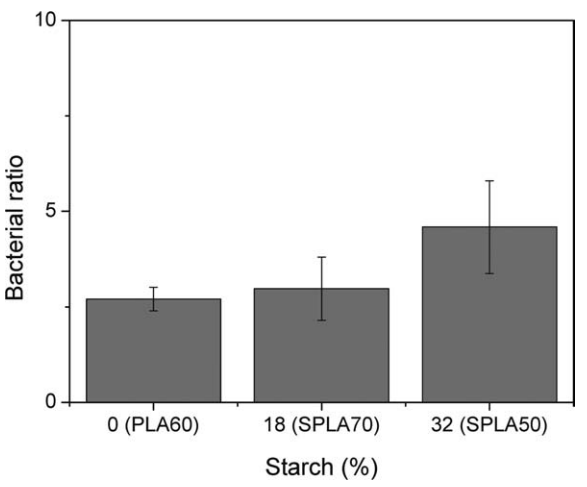

Figure 1 Bacterial ratio as function of % starch (0, 18, and 32%).

This study indicated (Fig. 1) that the bacterial ratio obtained after 10 and 2 weeks of experiment lifetime was not significantly different in the cases of PLA blends containing 0% (PLA 60) and 18% (SPLA 70) of starch but increased significantly in the case of 30% (SPLA 50) (*t*-test). The results suggested that the amount of starch might have been too low or simply not available at the polymer's surface for bacterial growth in the case of the blend containing 18% starch (SPLA 70). These results might be explained by the physicochemical properties of starch, namely crystallinity and hydrophobicity.[30] Usually, biodegradation occurs preferably in the amorphous regions of the polymer that have a higher mobility of the polymeric chains and therefore are more accessible to the microorganisms. Starch, being less crystalline than PLA, was more prone to microbial attack. In addition, the hydrophilic nature of starch, characterized by a higher number of hydroxyl groups in its structure as compared to the one present in PLA, promotes swelling and hydrolysis of the polymer matrix enhancing biodeterioration.[31] The effect of 18% starch-based thermoplastic in the biodeterioration potential of the PCL blend (SPCL 70) was also not significant (Table II), and the explanation is identical to the one of PLA blend (SPLA 70), as mentioned earlier.

FTIR analysis of polymeric blends was made before and after the biodeterioration assay. There are no significant changes in both spectra. One possible explanation for this result is that bacteria mainly attacked the surface of the polymer in the amorphous phase, and chain scission was not significant to be detected by FTIR.

Biodegradation of polymer particles by the BOD method

The biochemical oxygen demand of polymers (HDPE, PCL, and PLA) and blends (PCL 60, PLA 60, SPLA 50, SPLA 70, and SPCL 70) was determined in a closed respirometer (ISO 14851 (1999)) during 40 days. Biodegradability values were expressed as the amount of O_2 consumed during sample biodegradation divided by their theoretical

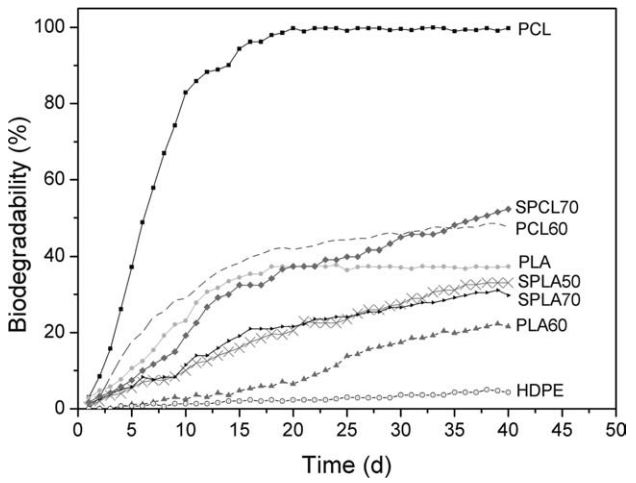

Figure 2 Percentage of biodegradation of the polymers and blends, without nitrification inhibitor, according to ISO 14851 (1999).

oxygen demand (ThOD) and are presented in Figure 2. The experimental results suggested that PCL was more biodegradable than PLA. A similar result was obtained in the case of the blends containing either PCL or PLA, being PCL 60 more biodegradable than PLA 60. The biodegradability of PLA was increased by the addition of increasing amounts of starch, and the same was observed for PCL. The HDPE's biodegradability was negligible compared to the other polymers and blends. The biodegradability of the PLA blend increased significantly by the addition of 18% starch (*t*-test) which was not observed in the case of the PCL blend. Further increase on starch in the PLA blend to 30% did not increase its biodegradability significantly. Results obtained by the BOD method are mostly in agreement with those obtained by the microbial growth method. Differences might be attributed to a reduced accessibility of microorganisms to polymers when present in the shape of polymeric film. Ammonium ions, present in the mineral medium used in the BOD method, are a source of nitrogen for the growth of carbon oxidizing microorganisms and, given sufficient time, might also be oxidized to nitrate by autotrophic microorganisms (nitrification process). This reaction does not contribute to the metabolism of organic carbon but consumes oxygen which is quantified in the method.[32] To assess the contribution of autotrophic ammonium oxidation to oxygen consumption, biodegradability of polymers and blends were also determined in the presence of allylthiourea (ATU), a specific inhibitor of the nitrification process. It was found a reduction of the biodegradability of polymers and blends in the presence of ATU, as depicted in Table III. These results suggested that in this study biodegradability determined in the absence of ATU is overestimated. In view of these findings, the use of ATU or the adjust of the C/N ratio present in the mineral medium to minimize oxygen consumption in the oxidation of ammonium ions in the BOD method was proposed.

To evaluate the extent of biodegradation of polymers (Fig. 3) and blends (Fig. 4), FTIR spectra of unbiodegraded and biodegraded samples were compared. FTIR spectra of PLA [Fig. 3(b)] and PCL [Fig. 3(c)] before and after biodegradation showed major changes that were not observed in the case of HDPE [Fig. 3(a)]. Transmittance data, on a common scale, showed that all peaks in FTIR spectra of PLA [Fig. 3(b)] decreased in size after biodegradation. Reduction in the CH-assymetric (2920 cm^{-1}) and CH-symmetric (2850 cm^{-1}) stretches indicated a decrease in PLA molecular weight while the reduction of peaks related to carbonyl (1800 and 1700 cm^{-1}) and ether (1100 cm^{-1}) suggested chain scission. A reduction of the peak at 1460 cm^{-1} was associated with the decrease of CH_3 side groups. A considerable change in the PCL backbone took place during the biodegradation process [Fig. 3(c)] resulting in a reduction of peaks related to CH bonds (3000–2800 cm^{-1}), carbonyl (1800 and 1700 cm^{-1}), and ether (1100 cm^{-1}). These results indicated chain scission

TABLE III
Biodegradation (BOD/ThOD) of Polymers and Blends (40 days Essay) Determined by the BOD Method With and Without Nitrification Inhibitor (Values Listed in the Table Are the Average ± 95% Confidence Interval)

Sample inhibitor	BOD (mg/L O_2)		ThOD (mg/L O_2)	BOD/ThOD	
	Without	With		Without	With
HDPE	103 ± 66	87 ± 36	4477	0.02	0.02
PCL	2522 ± 397	1683 ± 99	2527	1.00	0.66
PLA	597 ± 115	228 ± 99	1601	0.37	0.14
PLA 60	547 ± 132	427 ± 291	2527	0.22	0.17
PCL 60	1486 ± 175	1128 ± 695	3126	0.48	0.36
SPLA 50	1009 ± 133	388 ± 99	3050	0.33	0.13
SPLA 70	716 ± 289	506 ± 199	2401	0.30	0.21
SPCL 70	1446 ± 497	1169 ± 99	2766	0.52	0.42

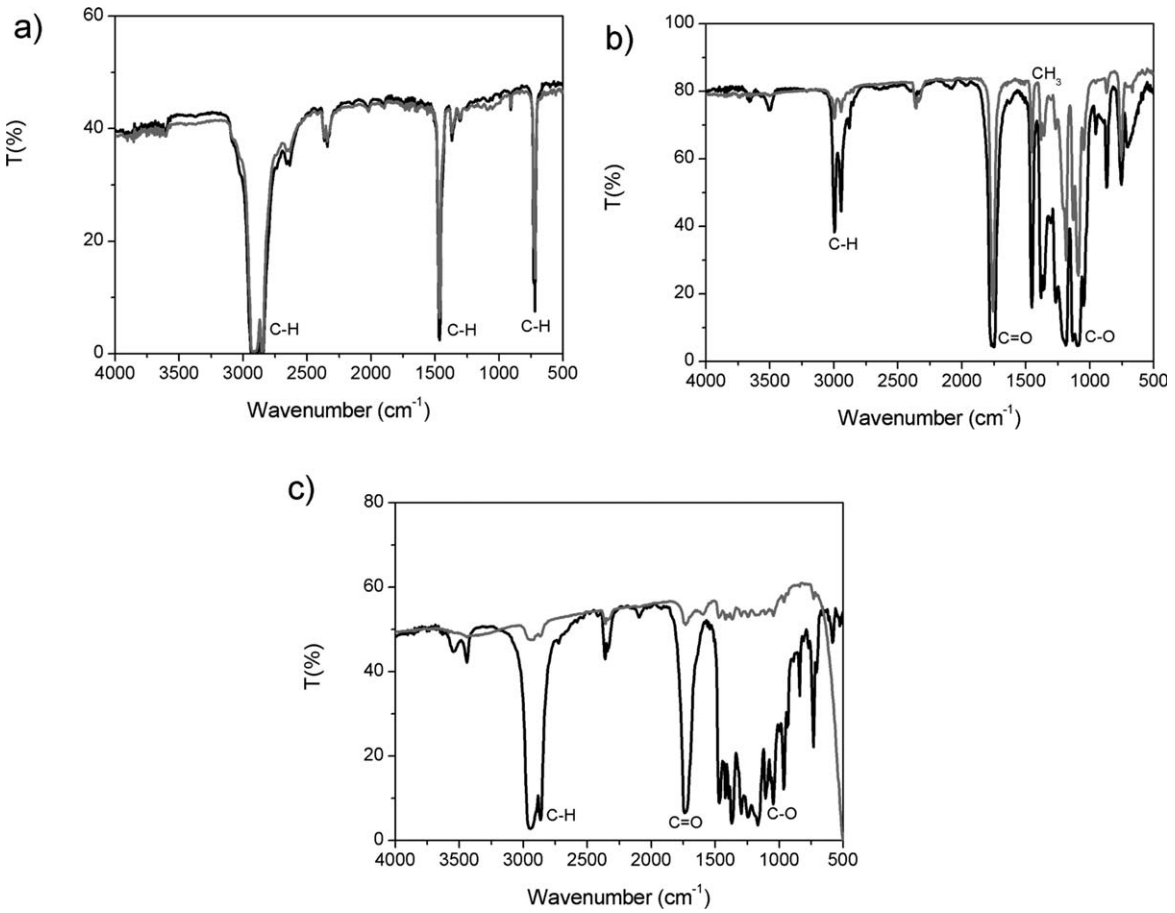

Figure 3 FTIR spectra of undegraded (black line) and biodegraded (gray line) polymers: (a) HDPE, (b) PLA, and (c) PCL.

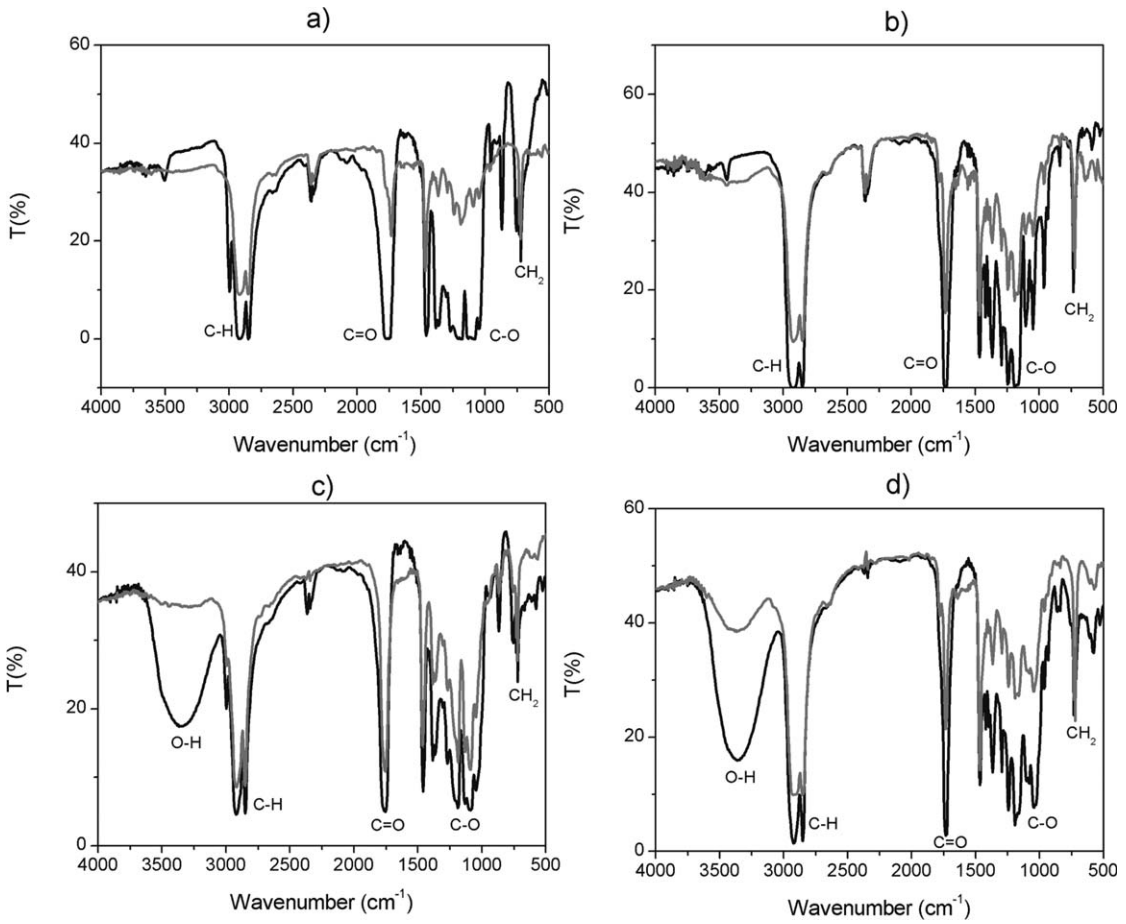

Figure 4 FTIR spectra of undegraded (black line) and biodegraded (gray line) blends: (a) PLA 60, (b) PCL 60, (c) SPLA 70 (18% starch), and (d) SPCL 70 (18% starch).

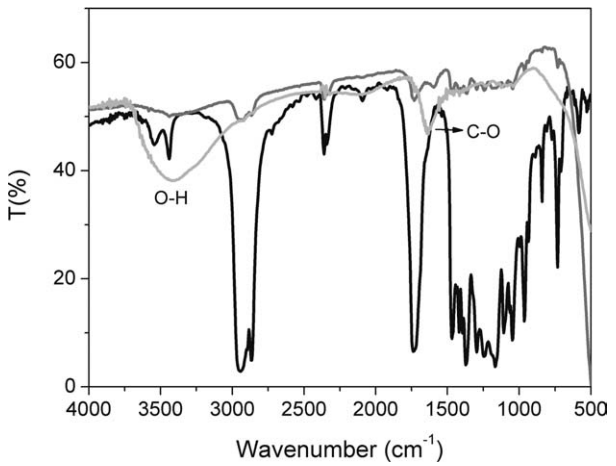

Figure 5 FTIR spectra of PCL undegraded (black line), biodegraded (dark gray line), and biodegraded in the presence of ATU (bright gray line).

and consequently a strong reduction of PCL molecular weight. Differences between unbiodegraded and biodegraded samples were noticed by visual analysis of the prepared films, the biodegraded was very brittle. FTIR spectra of PLA 60 [Fig. 4(a)] showed a significant reduction in all peaks related to PLA (as previously described) while the ones associated to HDPE, mainly the peak connected to CH_2 groups (720 cm^{-1}), were still present indicating that no major changes occurred in this polymer. In the case of PCL 60 [Fig. 4(b)] similar results were obtained. The spectra of undegraded blends containing similar amounts of starch, SPLA 70 [Fig. 4(c)] and SPCL 70 [Fig. 4(d)], showed the presence of OH peaks (3600 and 3200 cm^{-1}) that decreased in the spectra of biodegraded blends indicating bound scission probably due to a hydrolysis reaction.[33] As expected, a significant decrease of all peaks related to PLA and starch in SPLA 70 or PCL and starch in SPCL 70 were observed during the biodegradation process with the exception of the peak related to the CH_2 group of HDPE (720 cm^{-1}). The extent of biodegradation increased with the amount of starch present in SPLA blends (data not shown). In summary, the spectra of polymers and blends, after biodegradation, presented a significant reduction in the intensity of the peaks corresponding to the groups C—H, C=O, C—O, and O—H. This reduction might have been due to the metabolism of oxygen consumption microorganisms, as suggested by the BOD test. FTIR spectra of polymers and blends biodegraded in the presence of ATU showed a smaller reduction of the intensity of all peaks compared to one obtained in the absence of the nitrification inhibitor (data not shown). These results are complementary to the biodegradability data obtained for polymers and blends by the BOD method.

FTIR spectrum of PCL biodegraded in the presence of ATU presented a broad band at 3450 cm^{-1}, which is associated to O—H bonds (Fig. 5). A possible explanation for this result might be the formation of acid and alcohol groups due to PCL hydrolysis and reaction with protons (H^+) existing in the reactional medium.

Comparison with literature data

Table IV summarizes several studies performed to evaluate the biodegradability of PCL and PLA polymers. It is interesting to note that different shapes of polymers, biodegradability methods, experimental conditions, and length of the assays were used complicating the direct comparison of biodegradability data. For instance, values of 38%[18] and 80%[34] are presented for the biodegradability of PCL particles

TABLE IV
Summary on Literature Values of PCL and PLA Biodegradability

Polymer	Method	Biodegradability	References
PCL particles (188–200 μm) Mw = 43 kg/mol	Aquatic test – ASTM D-5209 (CO_2 evolution)	80% at 30°C after 11 days	34
PCL particles Mw = 80 kg/mol	Composting conditions –ASTM D-5338 (CO_2 evolution)	4.3%[a] at 58°C after 54 days	36
PCL particles Mw = 50 kg/mol	Composting conditions – ASTM D-5338 and ISO 14855 (CO_2 evolution)	21.6%[a] at 58°C after 46 days	8
PLA film starch powder	Composting conditions – ASTM D5338 and ISO 14855 (CO_2 evolution)	64.2% PLA at 58°C for 63 days	38
PLA film PCL film and particles	Aquatic test –ISO 14853 (O_2 consumption)	3.7% PLA film 34.8% PCL film 37.7% PCL particles at 30°C after 28 days	18
PLA film	Composting conditions – ASTM D-5338 and ISO 14855 (CO_2 evolution)	86% at 58°C after 58 days	39
PLA film	Composting conditions –ISO 14855 (CO_2 evolution)	55% PLA at 58°C after 90 days	37

[a] Calculated from the mass of CO_2.

by the Aquatic Test done at 30°C. In this study, using the same test and grinded samples, almost 100% was obtained without the addition of nitrification inhibitor and 66% with inhibitior at the same temperature. One of the several possible explanations for these highly variable results might be related to polymer properties: physical form (film or powder) molecular weight, molecular weight distribution, and crystallinity degree.[35] These data are usually not mentioned in literature studies. The data obtained in this study also suggests that the occurrence of nitrification (oxygen consumption in the oxidation of ammonium to nitrate and carbon dioxide production) might overestimate biodegradability results. The biodegradability essays done under composting conditions presented very distinct results, 4.3% for PCL with molecular weight of 80 kg/mol[36] and 21.6% for the one with 50 kg/mol[18], suggesting that biodegradability decreases with the increase of molecular weight. Despite of the higher temperature used in the biodegradation test under composting conditions (58°C), the biodegradability of PCL particles reported in literature was lower than the one obtained by the Aquatic Test as mentioned earlier. Conversely, literature studies indicated that PLA films were more biodegradable under composting conditions at higher temperatures (58°C), 55%,[37] 64%,[38] and 86%,[39] than at lower temperatures (30°C), 3.7%[18] used in the Aquatic Test. The fact that higher temperatures favor nonenzymatic hydrolysis of ester bonds[40,41] support the results obtained for PLA films. As a main conclusion, this study suggested that PCL is more biodegradable than PLA by the Aquatic Test.

Guidelines from the Organization for Economic Co-operation and Development (OECD) established that a test substance is regarded as "readily biodegradable" if the degree of biodegradation based on dissolved organic carbon removal is higher than 70% (OECD 1992). In the case of BOD determination or CO_2 production, 60% of the theoretical values have to be reached. This removal is required to occur in a specific assay with the test material as the sole carbon source, and within 10 d after the initial lag phase. According to the results obtained in this study, only PCL may be considered "readily biodegradable" according to the OECD standard, presenting an 83% removal within 10 d in the absence of inhibitor. However, these results do not comply with the definition of "readily biodegradable" established by the OECD guidelines. If a chemical does not pass the "ready"-level test, either degradation starts too late or it occurs too slowly. The results from the O_2 consumption test (Fig. 2) seem to indicate that biodegradation of the polymeric blends is a slow process.

CONCLUSIONS

The results obtained have shown that the blend containing PCL is more biodegradable than the blend containing PLA based on the microbial growth (ASTM G 22-76) and biochemical oxygen demand (ISO 14851:1999). Addition of starch increased the biodegradability of the PLA blend. The biodegradability of the blends evaluated in the presented study by the biochemical oxygen demand method ranged from 22% (PLA 60) to 52% (SPCL 70). Therefore they may not be considered "readily biodegradable" according to the OECD standard. The qualitative results of FTIR spectroscopy of unbiodegraded and biodegraded polymeric blends are in agreement with the ones obtained in the standard biodegradability tests.

Biodegradability of fine grinded polymeric blends was tested using the biochemical oxygen demand. It is important to point out that the surface area of the polymeric material sample available to microbial attack in the present study was increased considerably compared to film samples. Thus, the biodegradation under these conditions was enhanced when compared to tests performed in real environment.

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