Degradation of PLA and PLA in composites with triacetin and buriti fiber after 600 days in a simulated marine environment

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ABSTRACT: Poly(lactic acid) (PLA), the polymer object of this study, degrades by a biotic process after an abiotic hydrolysis process. Its degradation was evaluated after 600 days of exposure in a simulated marine environment (SME), as buriti fiber-reinforced composites having triacetin as coupling agent. Composites were obtained by extrusion and films were produced by compression molding. After between 60 and 600 days of exposure, PLA had a weight loss of 2.5%, PLA/T of 1.5%, and 10–12% of weight loss for PLA/B and PLA/B/T, respectively. PLA intercalates reduction, increase, and decrease of its crystallinity attributed to hydrolysis (up to 15 days), impairment of amorphous segments (45 days), and loss of integrity of the matrix (100–600 days), respectively. In the PLA/T composites, triacetin inhibited the diatom colonization process, having its crystallinity values increased after nearly 100 days of exposure with subsequent reduction. For samples with buriti fiber, changes in crystallinity were attributed to absorption of water and exposure of matrix amorphous segments. PLA degradation in a SME is evidently favored by the use of natural fibers since they make easier water access to the matrix and colonization by the protists group, diatoms, showing that the polymer can have reduced post-use shelf life as composites, with benefits while in use and at the same time post-use environmental benefits. Triacetin inhibits PLA colonization and degradation up to 45 days after exposure, after which it no longer influences the degradation process. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2016, 133, 43290.

INTRODUCTION

One of the present world's toughest issues is the unrestrained production of polymer resins which reached 300 million tons in 2013,[1] which, by being inert to degradation, spread out or pile in marine and terrestrial environments, contaminating fauna and flora.[2,3]

Nearly 8 million tons of polymer wastes are thrown into the oceans every year according to the authors of the survey "Plastic waste inputs from land into the ocean."[4] The researchers' team estimates that the amount of plastics thrown every year into the ocean could reach 17.5 million tons until 2025. The lack of treating systems and proper disposal for residues in general feeds the input of plastics into the ocean.[4]

One alternative for minimizing the problem of polymer accumulation in marine environment is the development of polymer artifacts based on biodegradable polymers. However, biodegradable polymers can have their properties and processability improved by the incorporation of fillers and additives which make possible to extend their useful life in certain applications. However, upon discarding, such polymers could have their properties modified as a result of exposure conditions so that they would take longer times to degrade than those conventionally observed.

Poly(lactic acid) (PLA) is a biodegradable thermoplastic based on natural resources such as starch from organic products including corn, sugarcane, potatoes, and beetroot.[5–9]

PLA is degraded by a hydrolysis reaction[10–12] which is usual for polyesters. The hydrolytic degradation mechanism occurs by diffusion of water toward the polymer interior, promoting scission of ester linkages, reducing chains into soluble fragments, and leading to lower molar mass.[13] The by-product formed in the PLA hydrolytic degradation process is lactic acid,[14] which is subsequently incorporated into cycles of carboxylic acids, carbon dioxide, and water. Polymer degradation by-products are then incorporated by microorganisms.[15] Mechanical and thermal properties as well as PLA processing properties can be

modified by the addition of fibers and other additives. Natural fiber PLA reinforcement seems to be a technically viable alternative with the aim of improving its mechanical performance while maintaining the end product environmentally planned.[16]

Natural fibers have many advantages relative to synthetic fibers, such as low density, low cost, relative ease of processing, and especially their recycling potential.[17,18]

Buriti (*Mauritia flexuosa*) is a robust, palm tree, with large leaves disposed as a fan and which is abundant in the North East region of Brazil. Buriti leaves are rich in cellulose and have relevant applications as polymers reinforcement filler.[19–22]

Two sorts of degradation can be considered during the immersion of a composite in an aqueous medium: physical degradation with plastifying effect and swelling by the medium and chemical degradation, induced by matrix hydrolysis and fiber degradation.[23]

Vegetable fibers have affinity with water molecules in view of their chemical composition and porous structure.[24] The aqueous environment can set forth intermolecular fibers surface interactions reducing adhesion of same with matrix,[25] causing delamination.[26]

Chen *et al.*[27] stated that enzymatic degradation occurs after long immersion delays, this phenomenon leading to loss of mechanical properties and consequently reduced vegetable fiber useful life in the composites.

In search for improving fiber–matrix interface leading to improvements in composite properties and processability, coupling agents are used. For the PLA and fibers composite, the literature mentions 5 wt % triacetin.[28,29]

In view of the above, the main goal of this work is the assessment of the influence of buriti fibers and triacetin on the degradation of PLA composites for different exposure times in SME through changes in physical, chemical, thermal, and morphological properties as compared with properties of neat PLA.

The experiment was performed in a simulated marine environment in an aquarium for fish, corals, and algae of the Caxias do Sul (RS/Brazil) Hospital, so as to comply with actual marine environment conditions which result in guaranteed quality of life and development of all its inhabitants. It was in this simulated environment that the degradation of PLA and of the composites with buriti fiber and triacetin was performed.

PLA degradation in a simulated marine environment is evidently favored by the use of natural fibers, showing that the polymer can have, when as a composite, benefits while in use, and lower post-use durability which leads to environmental benefits. The triacetin function is to assist in composite processing when fibers are incorporated, and this study, it inhibited colonization up to 45 days of exposure.

EXPERIMENTAL

For carrying out this study, PLA was supplied by Cargill (grade 3251 D) while triacetin was acquired from Sigma Aldrich. Buriti fiber as braids was supplied by Sisal Sul—Brazil. Macronutrients

sodium chloride, calcium, potassium, sulfur, and magnesium employed in the simulated marine environment were acquired from the Red Sea Company.

Preparation of Composites

Buriti braids were separated, milled in a MARCONI model MA 580 (Brazil) knife mill at 60°C for 12 h, washed under distilled water and dried in a MARCONI model MA 035 (Brazil) air circulating oven in agreement with the methodology described by Gupta *et al.*[30] and Van Den Oever *et al.*[31]

PLA, PLA composites with buriti fiber (30 wt %) designed as PLA/B, triacetin-containing PLA (5 wt %) designed as PLA/T and PLA with triacetin (5 wt %) and buriti fiber (30 wt %)designed as PLA/B/T were extruded in a SEIBT ES35 F-R (Brazil) single-screw extruder at screw rotation speed of 42.88 RPM, length/diameter ratio (L/D) of 32 and compression ratio (CR) 2.5. The temperature profile was $Z_1 = 120°C$, $Z_2 = 165°C$, and $Z_3 = 180°C$. The extruded mass was milled in a MARCONI knife mill, of temperature profile $Z_1 = 120°C$, $Z_2 = 170°C$, $Z_3 = 175°C$, $Z_4 = 175°C$, $Z_5 = 180°C$, $Z_6 = 165°$, $Z_8 = 170°C$, and $Z_9 = 175°C$ under open matrix. The extruded product was milled, dried and compression molded in a SCHULZ PH5 15T (Brazil) press for 60 s, at a temperature of 180°C in order to obtain films. Test specimens were cut from the produced films, the dimensions of which were 200 × 100 mm^2 and 1 mm thickness.

Simulated Marine Environment

The simulated marine environment used in the degradation tests is at the Caxias do Sul University UCS-Aquarium/Brazil and has the following dimensions: volume, 250 L, dimensions 580 × 1100 × 500 mm. It is a head-aquarium, with fixed parameters for water temperature (22–25°C) and pH (between 7.9 and 8.5), as defined by the presence of experimental fish, algae, corals, crustacean, plankton, and microorganisms. Simulated marine environment conditions were not altered in order to comply with specific requirements of polymer degradation simulation in a marine environment. The medium macronutrients are: sodium chloride, calcium, potassium, sulfur, and magnesium and comprise approximately 99% of the total nutrients.

The remaining 1% micronutrients include: bromine, boron, carbon, nitrogen, fluorine, silicon, and strontium. The aquarium is provided with 7 lamps (2 yellow, 3 white, and 2 blue), which are equivalent to 250 W, simulating ultraviolet (UV) rays on the aquarium. Withdrawal of samples was performed after 15, 30, 45, 60, 100, and 600 days of exposure. Each withdrawn sample was washed with distilled water and then left in a dessicator for 24 h. Samples were weighed in an analytical scale and their mass was assessed before and after withdrawal.

Test specimens for degradation analyses at different periods were placed in the simulated marine environment as experimented in the Aquarium Hospital of the University of Caxias do Sul—UCS Aquarium.

Morphological Characterization of PLA and Composites Films

The morphological characterization of the fractured sample surface was performed in a SHIMADZU SSX-550 scanning electronic microscope (SEM) with disperse energy spectroscopy (DES) (Japan) operating at 10 kV.

Analysis of PLA and Composites Films Chemical Changes

Analysis of chemical changes were monitored by Fourier Transform Infrared Spectroscopy (FTIR) in a Thermo Nicolet, model IS10 instrument, on prepared films by the KBr pellet method, in the wave number range of 4000 to 400 cm^{-1}. Lactic acid index (I_{LA}) was calculated as the ratio between band surfaces A_1 (3200 cm^{-1})[32,33] and A_2 at 750 cm^{-1}, which is considered one of the PLA bands[34,35] [eq. (1)].

$$I_{LA} = A_1/A_2 \qquad (1)$$

The band at 3200 cm^{-1} can be credited to the formation of lactic acid and/or pyruvic acid as hydrolysis products, an indication of PLA degradation. The absence of a large, strong intensity band in the region of 3700–3050 cm^{-1} (OH group stretching, which is characteristic of carboxylic acid and alcohol which make up lactic acid) evidences the absence of PLA hydrolysis products such as lactic acid and/or pyruvic acid.[32,33]

Thermal Characterization of PLA and Composites Films

Differential exploratory calorimetric analysis (DSC) was performed on samples of approximately 10 mg, on standard aluminum pans using a Mettler-Toledo DSC882 (USA) scale under nitrogen atmosphere at 50 g min^{-1} flow, heating rate of 10°C min^{-1}, the sample being heated from 20 to 200°C and kept at 200°C for 3 min in a single run. One focus of this study is to evaluate the crystallinity index (X_c) of this product, it being measured by the enthalpy of fusion of the first DSC run since it is this information which leads to the actual crystallinity of the product, without eliminating the effects of the promoted processing. The PLA crystallinity index (X_c) was determined by eq. (2).

$$Xc \ \% = (\Delta Hm + \Delta Hc) \times 100/n \times \Delta H° \qquad (2)$$

where ΔHm and ΔHc (J g^{-1} of the polymer) are the enthalpies of fusion and cold crystallization, respectively, read from the thermogram and $\Delta H°$ is the enthalpy of fusion of hypothetically 100% crystalline PLA, the value 93.1 J g^{-1}[23,36] being fixed and n being the PLA mass percent in the composite.

Analysis of Residual Mass of PLA and Composites Films

The samples residual mass (M_r) was determined by eq. (3), mi being the initial mass (g) and m_f the final mass (g) determined by eq. (3).

$$Mr = \left(\frac{mf}{mi}\right) \times 100 \qquad (3)$$

RESULTS AND DISCUSSION

Morphological Characteristics of PLA and Composites Films before and after Exposure

The morphology of PLA and of the composites (PLA/B, PLA/T, and PLA/B/T) after different exposure days (15, 30, 45, 60, 100,
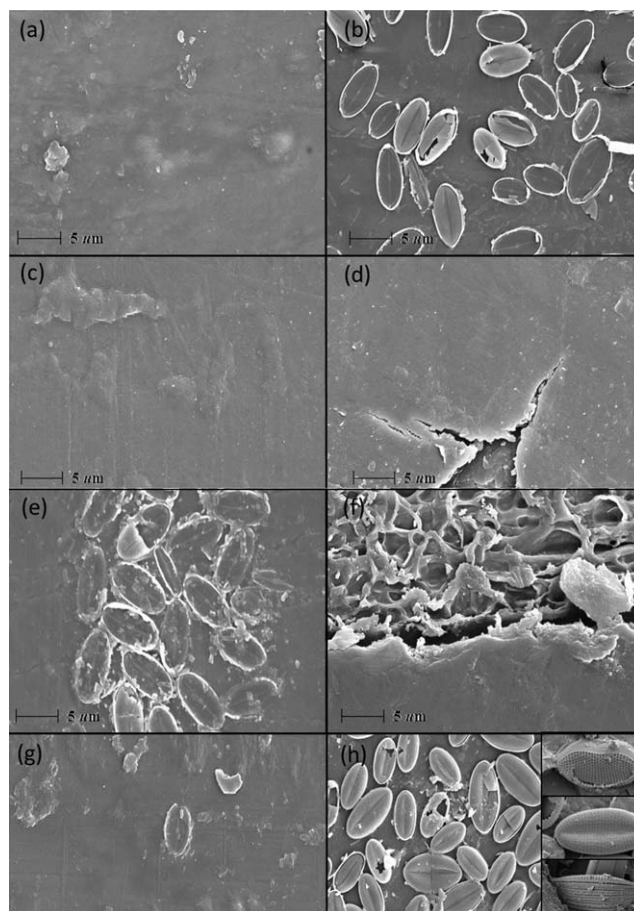

Figure 1. SEM micrographs of compression molded films (a) PLA, (b) PLA/B, (c) PLA/T and (d) PLA/B/T, after 15 days and (e) PLA, (f) PLA/B, (g) PLA/T, and (h) PLA/B/T, after 30 days of exposure in a simulated marine environment.

and 600) in a simulated marine environment is presented in Figures 1–3.

It could be observed that after 15 days of exposure in a simulated marine environment the composite with buriti fiber (PLA/B) showed colonization by the protists group, the diatoms. PLA and PLA/T did not show evidence of environmental action on the films. In PLA/B/T composites, some content was removed, with holes in the film being attributed to fiber withdrawal. The buriti fiber rough morphology enables water to penetrate[37] and consequently getting access to the PLA matrix.

After 30 days of exposure to simulated marine environment the PLA colonization could be observed, with withdrawal of a portion of buriti fiber in the case of PLA/B caused by water absorption and swelling[38]; in this figure different kinds of diatoms and other nonidentified microorganisms can be observed during colonization of PLA/B/T films and also the beginning of the PLA/T film colonization. It was concluded that the inclusion of buriti fiber into composites promoted microorganisms' colonization on the samples surface and consequently, resulting in an ease of water absorption by the fiber, enabling the PLA from the composites to evidence degradation in shorter times than those observed for pure PLA.
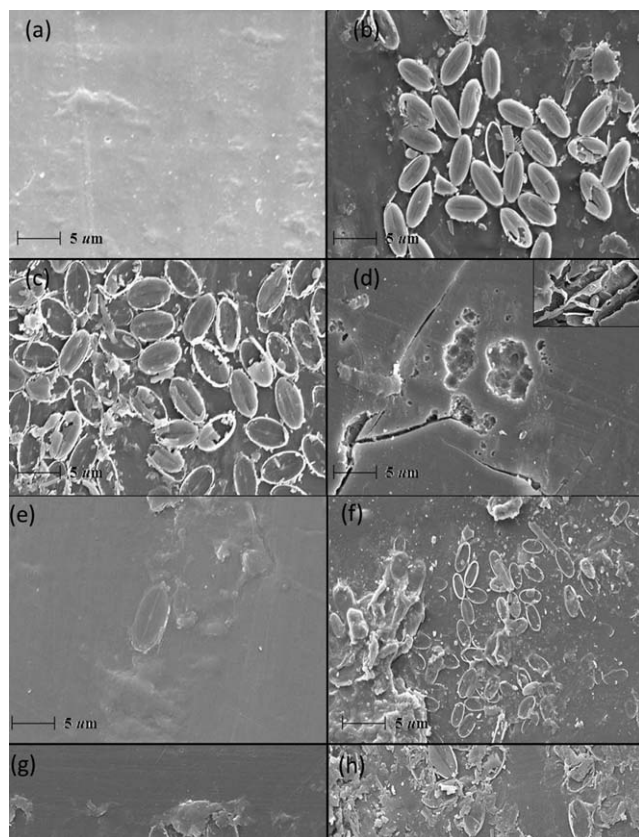
Figure 2. SEM micrographs of compression molded films (a) PLA, (b) PLA/B, (c) PLA/T and (d) PLA/B/T, after 45 days and (e) PLA, (f) PLA/B, (g) PLA/T, and (h) PLA/B/T, after 60 days of exposure in a simulated marine environment.

Triacetin is used as a cellulose plasticizer, in the manufacture of cosmetics, as a vehicle in fungicides compositions or as a modifier of barrier properties, being related to permeability to water vapor, gases and aromatic components.[39] Being a small molecule it is easily coupled among polymer chains.[40] In this study,
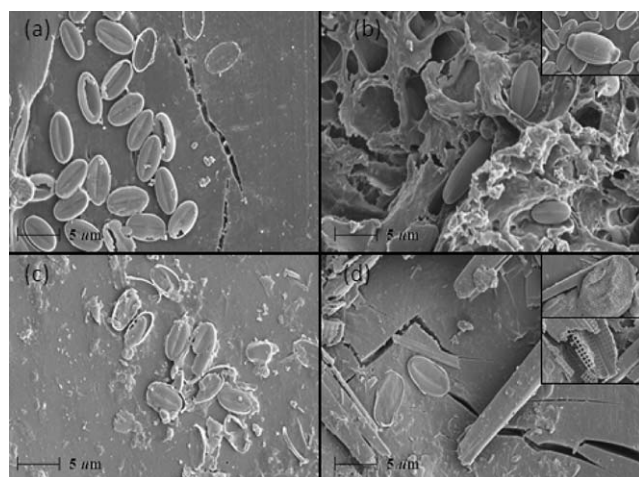

Figure 3. SEM micrographs of compression molded films (a) PLA, (b) PLA/B, (c) PLA/T, and (d) PLA/B/T, after 100 days of exposure in a simulated marine environment.
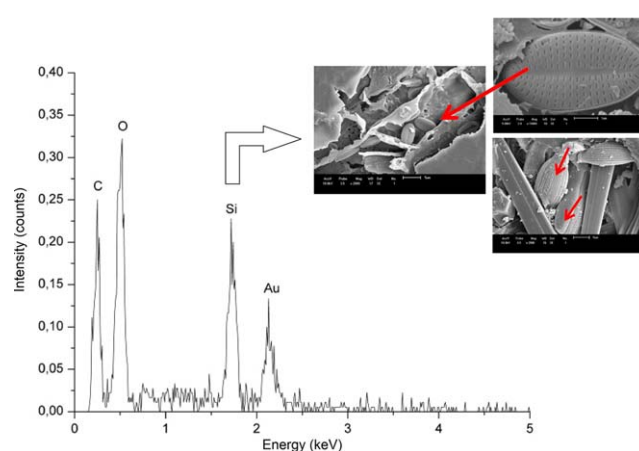

Figure 4. Composites SEM micrograph pointing out the presence of different diatoms on buriti fibers and EDS for diatoms in a simulated marine environment after 100 days exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

it was employed as a coupling agent, and it inhibited film colonization in a marine environment for 30 days. Diatoms are unicellular algae organisms that have siliceous structures. These can move on a substrate secreting mucilaginous substances and are mainly constituted of acidic polysaccharides which can be carboxylated and/or sulfated in different degrees.[41]

After 45 days of exposure in a simulated marine environment (Figure 2), loss of integrity of the PLA matrix can be observed as a result of the action of algae and fiber removal promoting the presence of holes and cracks. The coupling agent, triacetin, does not any longer inhibit microorganisms' colonization after this period of exposure, this being attributed to matrix integrity loss by exposing the agent.

Upon 60 days of exposure, the observed behavior was similar to that reported for 45 days, the accumulation of biological material forming biofilms which tend to increase with exposure time.

Upon 100 days of exposure to the environment (Figure 3), the fiber composites (PLA/B) presented the most accentuated degradation caused by matrix integrity loss, fiber removal and diatoms positioned within the remaining fibers. This has not been evidenced by PLA and PLA/T. The PLA matrix, as well as the PLA/B/T specimen showed cracks in their surface.

Different kinds of diatoms (different frustules) were evaluated after 100 days of exposure in a simulated marine environment (Figure 4), on the buriti fiber samples (PLA/B and PLA/B/T). The same figure shows the energy dispersion X-ray spectroscopy (EDS) for diatoms residues evidencing silicates in their constitution.

The diatoms present in marine environments colonize surfaces of the existing polymers in that environment, chiefly where there are rough surfaces.[42]

On the basis of the study entitled "The plastic-associated microorganisms of the North Pacific Gyre,"[42] it was possible to identify the existing diatoms in our research. Diatoms of the classes
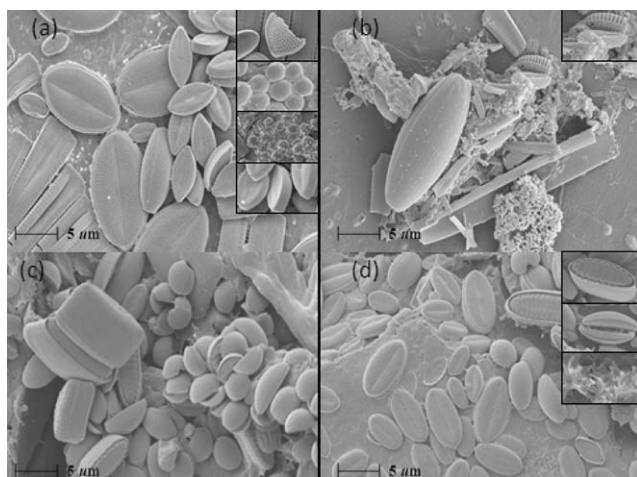
Figure 5. SEM micrographs of compression molded films (a) PLA, (b) PLA/B, (c) PLA/T, and (d) PLA/B/T, after 600 days of exposure in a simulated marine environment.

Bacillariophyceae, Fragilariophyceae besides centered diatoms among many others, each class having a different shape was identified.

After 600 days of exposure in a simulated marine environment (Figure 5), all the samples showed colonization by different microorganisms and loss of matrix integrity leading to fragility of samples. PLA is insoluble in water when its molar mass is sufficiently high, but when subjected to degradation, as in this study, being favored by the buriti fiber and triacetin and from 45 days of exposure on, water penetrates into its matrix and leads to hydrolysis of the ester groups, preferentially compromising the links of the polymer amorphous phase.[43,44]

Residual Mass of PLA and Composites Films before and after Exposure

The PLA and PLA/B, PLA/T, and PLA/B/T composites residual mass versus different exposure days (15, 30, 45, 60, 100, and 600) in a simulated marine environment can be seen in Figure 6.

For PLA, mass increase was attributed to the colonization by algae of the classes *Bacillariophyceae, Fragilariophyceae*, and centered diatoms among others, up to 60 days of exposure, where
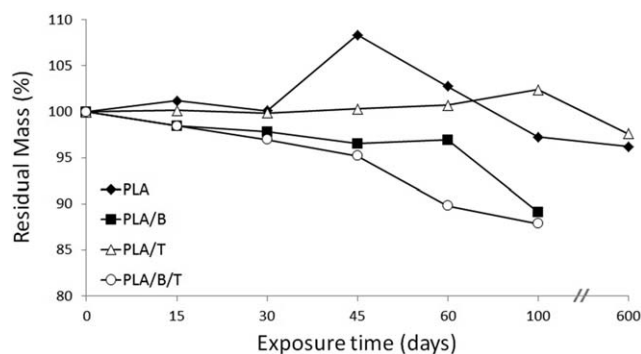

Figure 6. Residual mass, average mass of three test specimens, for PLA and PLA/B, PLA/T, and PLA/B/T composites versus different exposure days in a simulated marine environment.
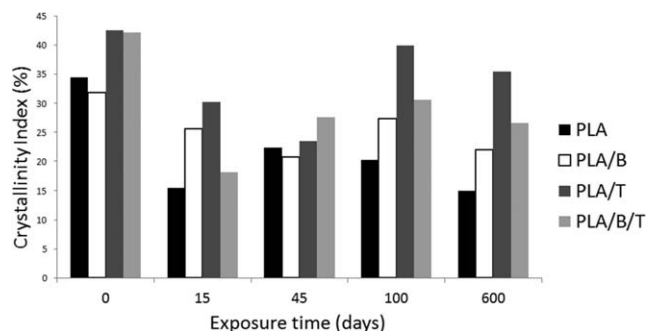

Figure 7. Crystallinity index for PLA and the PLA/B, PLA/T, and PLA/B/T composites versus different exposure times in a simulated marine environment.

the biofilm formation made it possible for changes to occur on the surface and having as consequence loss of material integrity.[45] Between 60 and 600 days of exposure in a simulated marine environment PLA had a loss of around 2.5% mass.

The coupling agent, triacetin, inhibited colonization up to nearly 45 days of exposure[39] evidencing mass increase after this period. Mass loss of the order of 1.5% was evidenced between 100 and 600 days of exposure.

Buriti fiber samples (PLA/B and PLA/B/T) evidenced mass losses of the order of 10–12% for PLA/B and PLA/B/T respectively. It is believed that mass loss is actually higher than this figure since microorganisms' colonization promotes sample mass increase. PLA/B and PLA/B/T samples did not resist to 600 days of exposure, they broke. It can be concluded that the buriti fiber in PLA composites favored their degradation at times lower than those observed for PLA, since it makes easier for water to enter the matrix, with the consequent hydrolysis reactions which ultimately lead to product degradation. PLA hydrolytic degradation in an aqueous medium proceeds more rapidly at the surface, suggesting that hydrolysis products formed close to it are dissolved in the middle of the composite while in the inner portion there is a high concentration of terminal carboxylic groups able to catalyze ester hydrolysis.[46]

Thermal Characteristics of the PLA and Composites Films before and after Exposure

Figure 7 shows the crystallinity index for PLA and the PLA/B, PLA/T, and PLA/B/T composites versus different exposure times in a simulated marine environment.

The general analysis of the samples reveals that the crystallinity index shows similar behavior as relates to crystallinity, considering the specificities of each sample. It could be observed that after short exposure time's crystallinity index is reduced as a result of the microorganisms' colonization, water penetration into the matrix and plasticizing effect promoted by water. After a certain exposure period, crystallinity tends to increase. Such increase could be associated to attack of PLA amorphous regions, so that the remaining sample acquires higher crystallinity index. Finally, there is another reduction in crystallinity index as a result of the matrix integrity loss and compromising of the remaining crystalline segments.
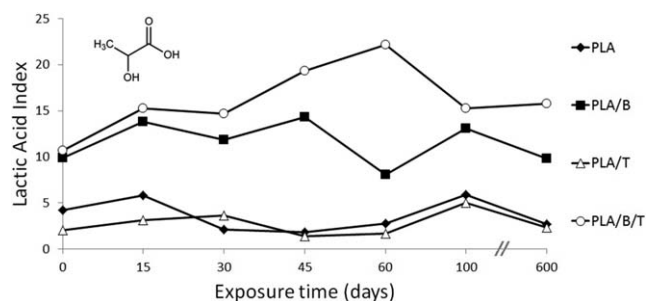
Figure 8. Lactic acid index (I_{AL}) for PLA and for PLA/B, PLA/T, and PLA/B/T composites versus different exposure times in a simulated marine environment.

For PLA, with initial X_c of 34.5% there was crystallinity reduction when assessed after 15 days of exposure. In this period, the sample did not show any microorganisms' colonization, therefore X_c loss is attributed to the presence of water in the matrix and exposure of amorphous segments to the medium.

After 30 days of exposure PLA colonization, it could be observed colonization on PLA; therefore, crystallinity increase observed at 45 days was attributed to the compromising of amorphous segments; thus, the remaining material becomes more crystalline. Upon longer exposure times, PLA crystallinity loss was attributed to matrix integrity loss in a general way.

For the PLA/T sample, which inhibited the diatoms colonization process until 45 days of exposure, it showed crystallinity loss up to this period, and increased values near 100 days of exposure with further reduction. It could be observed that the coupling agent added to PLA/T (42.5%) and PLA/B/T (42.1%) samples provided the highest samples crystallinity figures before exposure. Its action as coupling agent was not evaluated by SEM in view of the buriti fiber feature of being rough and porous and losing integrity by water action which hinders matrix/fiber interface evaluation.

The behavior of buriti fiber-containing samples was similar to that reported for the remaining samples; however, changes in crystallinity are attributed preferentially to the fact that samples absorb water allowing it to access the matrix, with the consequent easiness for microorganisms' action and exposure of amorphous segments.

Chemical Changes of PLA and Composites Films before and after Exposure

Figure 8 is a graph showing lactic acid index (I_{AL}) monitored by FTIR in the region of 3050–3700 cm^{-1}, this interval being wider than that suggested for identifying the PLA degradation by-product, lactic acid (3000–3500 cm^{-1}), this being due to the feature of the observed band to overlap other bands of interest. Stretching of the OH group was monitored, this group being characteristic of carboxylic acid and alcohol, which form lactic acid (the chemical formula of which is indicated in Figure 8).[46] A band in this interval also characterizes the OH resulting from water absorption by the samples, at 3000 cm^{-1}, overlapping the 3200 cm^{-1} band, which is of interest for the present study.

In order to evaluate PLA and composites behavior in a simulated marine environment, physical degradation with plasticizing effect and swelling by the action of the medium besides chemical degradation induced by matrix hydrolysis should be considered.[23]

By taking into consideration these types of degradation, it can be observed that for up to 15 days of exposure the samples behavior was similar, which is attributed to the effect of the presence of water, causing physical degradation, the buriti-containing samples having higher values of I_{AL}.

In the same period, Triacetin inhibits water inlet and consequently degradation of the PLA/T sample which is seen by low I_{AL} values which were confirmed by SEM analyses.

The same behavior observed for PLA/T was repeated for PLA. From 45 days on, keeping up to 60 days of exposure, PLA showed cracks and holes in the matrix, which could be evidenced by SEM, with loss of integrity, which favored microorganisms' colonization. During this period, PLA had diminished crystallinity (Figure 7).

The behavior of the fiber composites (PLA/B and PLA/B/T) was similar during the period of evaluation undertaken in this study, exception made to the collection of the PLA/B sample after 60 days. The augmented PLA composites degradation values were attributed to the PLA/B/T sample mainly in view of the presence of fiber and by the fact that from 30 days on, triacetin no longer influences the degradation process. By being a low molar mass structure, triacetin[40] can be removed preferentially from the matrix by environment action and fiber withdrawal, since the same showed fragility and loss of integrity from 30 days on, evidenced by SEM, reducing the adhesion of same to the matrix[25] causing delamination.[26] Diatoms colonization as evidenced by SEM corroborated the results observed by FTIR.

Chemical degradation induced by matrix hydrolysis with lactic acid formation, ascertained to the OH group stretching which is characteristic of carboxylic acid and alcohol[23] occurs from 45 days on of exposure in a simulated marine environment.

Diatoms colonization observed by SEM followed the matrix swelling reactions and hydrolysis at different periods of this study, however, were preferably located on the buriti fiber exposed by water action.

The seven lamps placed on the aquarium simulating ultraviolet rays (UV) could be responsible for the samples photochemical degradation, however this analysis was not performed since it is believed that the photochemical effect occurred for all of the exposed samples and that action of water and presence of buriti fiber have had a more significant effect on degradation of PLA.

CONCLUSIONS

Microorganisms could be directly involved in composites degradation since buriti fiber favored colonization of same on films surface at periods of time lower than those observed for PLA. Triacetin used as processing aid and coupling agent inhibited colonization up to 45 days of exposure, and after this period no longer influenced the composite degradation. The presence of

algae of the *Bacillariophyceae Fragilariophyceae* class and centered diatoms among other, superficially and within the fiber seems to affect composites' structure, a process favored by water absorption followed by hydrolysis. PLA degradation in a marine environment is evidently favored by the use of natural fibers, showing that the polymer can have, when as a composite, benefits while in use, and lower post-use durability which leads to environmental benefits.

ACKNOWLEDGMENTS

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