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Polyethylene / amphiprotic blends as alternative for decreasing plastics residues in the environment

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Summary

This work evaluated the biodegradation of polyethylene and amphiprotic starch blends in the presence of the fungi *Phanerochaete chrysosporium* (Ph) and *Talaromyces wortmannii* (BM-10). The mechanical properties of the blends decreased in function from the time of exposure to these fungi. The reduction of the mechanical strength was caused by the consumption of the starch constituent of the polymeric matrix, favoring the growth of the fungi. The production of CO_2 by the fungi, reinforces the theory that the starch was consumed as a source of carbon yielding carbon dioxide and other by-products. Hence, the consumption of starch by these fungi is responsible for the partial degradation of the blends.

Introduction

The wide use of polymeric materials in several applications is strongly related to their properties such as morphology, mechanical and thermal characteristics. The main problem that results from the accelerated use of these materials is related to the low degradation rate of those materials when dumped in landfills. Their disposal can cause serious problems in maintaining the environmental balance.

Alternatives are sought to substitute the conventional polymer in order to obtain materials that are more compatible with the philosophy of preserving the environment. One of the solutions has been the development of new formulations of plastic materials and the understanding of the mechanism that induces polymer degradation. This includes considering some aspects that can interfere in the biodegradation such as: chemical structures, pH, temperature, polymeric morphology, presence of additives and the types of microorganisms involved [1].

Plastics made of a mixture of starch and synthetic polymers constitute an alternative for decreasing these material's residues in the environment. Preliminary studies show that the removal of the starch, in the mixture polymer/starch, alters the physical properties of the plastic, facilitating the physical disintegration in the atmosphere and, consequently, their biodegradation [2]. However, to enable the polymer to be degraded in the environment, there are certain conditions to be met and it is necessary

to have the proper microorganisms which are the agents of the process. A polymer used in certain applications, is considered to be biodegradable if it degrades in the environment that would constitute its final destination. Therefore, the method used to evaluate its biodegradability should take in to account the environment in which the polymer will be disposed of [3].
Fungi are mainly responsible for the biodegradation of polymers, especially when the polymer consists of natural materials, such as starch and cellulose. Fungi degradation capacity occurs because they produce enzymes that hydrolyze the substrates that are their nutritious materials. This process is an aerobic process in which CO_2 is released into the atmosphere and nitrogen compounds and other substances are returned to the soil [3].
Many authors have researched the biodegradation of natural and synthetic polymers and their mixtures, due to the action of pure cultures and mixed cultures of microorganisms. This shows the scientific community's level of interest in this matter [4-7].
The identification of a new strain of fungi, and the use of mixed cultures, as well as their evaluation as polymeric biodegradation agents are of great importance in the reduction of the degradation time of those materials in nature.
The main objective of this work is to evaluate the biodegradation of low density polyethylene/amphiprotic starch blends using the fungi *Talaromyces wortmannii* and *Phanerochaete chrysosporium* as degradation agents. The use the modified starch in the blends is also important in the investigation of its properties and biodegradability, because only a few of the previous researchers used modified starch in the composition of the blends.
The importance of the study into low-density polyethylene (LDPE) biodegradable formulations is motivating much research in this area [8]. Polyethylene is used in several applications owing to its excellent properties, such as elasticity and flexibility.
We used the amphiprotic starch because this starch that contains in its structure a cation (N^+) and an anion (P^-). Then given credit that the blends composed of the LDPE and amphiprotic starch contend other nutrients such as phosphorus and nitrogen might contribute to the partial degradation of the blends by fungi.
The choice de fungus is another important aspect in the study of the polymeric biodegradation. The fungus must be capable to degrade molecules great and they has existed in large abundance in the soil. Example this fungi are the *Phanerochaete chrysosporium* known for degradation the lignin and it has been used in works concerning with the biodegradation of polymeric blends [9-11]. Example the common fungus of the existent in soil is the *Talaromyces wortmannii*.

Experimental

Polymers

A low density polyethylene (LDPE) polymer was used; it was supplied by BRASKEM. The amphiprotic starch was provided by Corn Products of Brazil.

Microorganisms

A strain of *Phanerochaete chrysosporium* (Ph) from the culture collection of the Federal University of Rio de Janeiro- Brazil and a wild strain of *Talaromyces*

wortmannii (BM-10) isolated from the soil of the Muribeca Landfill Site (Jaboatão dos Guararapes – PE - Brazil) were used. The latter fungus was identified in agreement with Stolk & Samson [12].
The *Phanerochaete chrysosporium* (Ph) strain was chosen because it has been reported in many works involving the biodegradation of polymeric blends [13]. The *Talaromyces wortmannii* strain (BM-10) was selected because it is a non-pathogenic fungus, while the other isolated strains from the landfill soil were all pathogenic.

Maintenance of the fungus cultures

The fungi strains were maintained in a Sabouraud–agar medium of the following composition: peptone (10g/L), glucose (40g/L), NaCl (7.5g/L), meat extract (3.5g/L), agar (12g/L), distilled water (1L). The pH was adjusted to 4.5 and the sterilization was accomplished at 121°C for 20 minutes. The strains were stored at 5°C.

Film Processing

In this study LDPE/starch blends were used in a 80/20 proportion (w/w), mixed by fusion in the mixture chamber of a HAAKE 90 rheometer, under the following conditions: control temperature: 140°C; maximum torque: 50 Nm; rotor velocity: 50 rpm; total mixing time: 10 min. The LDPE/starch blend resins, processed in the rheometer, were ground and compressed in a hydraulic press.

Biodegradation of the blends

Sturm test

The CO_2 production in the biodegradation process for the Sturm test consisted of a composed system of an air compressor, a reactor and two CO_2 collectors placed upstream and downstream from the reactor respectively. The test was realized in triplicate. In each system the collectors contained 400 and 200mL of barium hydroxide solution (Figure 1) [3]. The whole system was connected by hoses. 500 mL-Erlenmeyers were used as collectors and reactor. A 200mL of Sabouraud medium and one blend with a thickness of 0.17 ± 0.02mm were placed in each reactor. After agitating for 24h, in the absence of contamination, it was inoculated with the fungi mixed culture.

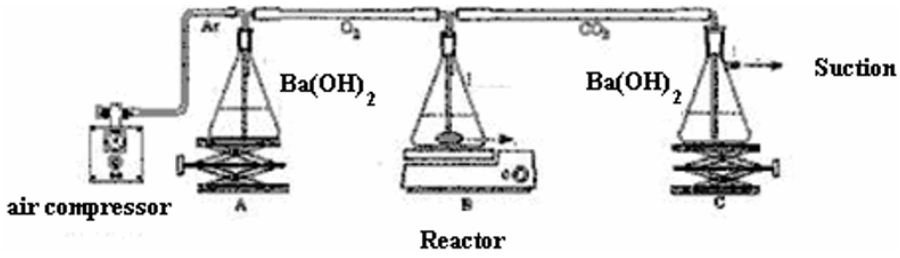

Figure 1. Equipment used to capture the dioxide of carbon.

Every 24 hours, the last recipient of the system was substituted for another containing a fresh barium hydroxide solution. The content of the substituted collector was

filtrated under vacuum. The filtrated material was neutralized with HCl 1M to determine the CO_2 production by difference. This process was done by the determination of the $Ba(OH)_2$ in excess, and obtaining the $Ba(OH)_2$ precipitated as $BaCO_3$ which was directly proportional to the CO_2 produced (equations 1 and 2). The system was monitored for 90 days.

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 \downarrow + H_2O \quad (\mathbf{1})$$

$$Ba(OH)_2 \text{ (excess)} + 2HCl \rightarrow BaCl_2 + 2H_2O \quad (\mathbf{2})$$

After biodegradation the test samples were disinfected with ethanol and dried.
A standard test was also done in a similar way without addition of the blends to the biodegradation test.

The blends biodegradation follow-up

The biodegradation follow-up was carried out, in accordance with the methodology described in the ASTM D 5247-92 [13] and Lee *et al*. [14], in the following steps: standardization of the samples of the polymeric films; disinfection and drying of the samples; transference of the samples to Erlenmeyer flasks containing the specific growth medium (Sabouraud liquid); agitation of the flasks at 200 rpm for 24 hours at room temperature; inoculation with the suspensions of fungi spores; disinfection and drying of the samples after biodegradation.
The test was monitored in triplicate for 165 days. The biodegradation activity evaluation for the mixed fungi culture in the polymeric blends was carried out using mass variation, a Differential Scanning Calorimeter (DSC), a Scanning Electron Microscope (SEM) and mechanical properties.

The blends biodegradation evaluation

Mass Variation

The evaluation of the average weight of the polyethylene/starch blend samples during the biodegradation process was carried out, weighing the samples before and after the test using an analytic scale model AND (HR-120).

Mechanical test

The mechanical tests were conducted in an EMIC DL 500 MF universal testing machine, observing the ASTM D 638-82a, in which the tensile strength and elongation at rupture percentage were determined [15].

Scanning Electron Microscope (SEM)

The blend morphologies before and after 90 and 164 days exposure to the microorganisms were examined using a JEOL JSM-5600LV microscope with 100, 500 and 1000 amplification lenses.

Statistical analysis

The data was analyzed using the program STATISTIC 22 [16]. Significance was determined at the 5% level.

Results & Discussion

Evaluation of the blends biodegradation

Mass variation of the LDPE / amphiprotic starch blends

Figure 2 shows blend weight of LDPE/amphiprotic starch in function of the time of the biodegradation. It was observed that the masses of the blends tend to be larger after exposure to fungi, except for the 30, 60 and 165 days exposure samples that presented little mass variation. The increase of the blend masses is related to the presence of microorganisms in the polymeric matrix. The microorganism cell mass accumulating on the films made it difficult to determine the real average weight of the blends after the degradation process.

This result is in agreement with El-Shafei *et al*. [17] who evaluated the ability of fungi and *Streptomyces* species to attack degradable plastics was investigated in pure shake-flask culture studies. They showed the changes after cultivation, such as the polyethylene/starch blends' average weight.

According to Arvanitoyannis *et al*. [18], the degradation of the LDPE/starch blends is related to the accessibility of the microorganisms to the starch. Although the ability of the microorganism to attack starch is influenced by various factors, such as their number, mobility and reproduction rate, in general, the kinetics of the degradation of the blend follows three phases: 1 – The amorphous starch chains, to which access is easily gained by the microorganisms, are usually located near the surface. The penetration of microorganisms into the interior of the LDPE/starch blend can be explained by the percolation theory; 2 – Invasion by microorganisms, while the starch chains that remain unaffected by the microorganisms remain; 3 – Degradation approaches the final stage, as the number of microorganisms diminishes due to the shortage of nutrients. The huge surface area generated by the removal of starch from the blend increases the process of chemical degeneration, which in turn favors the biodegradation.

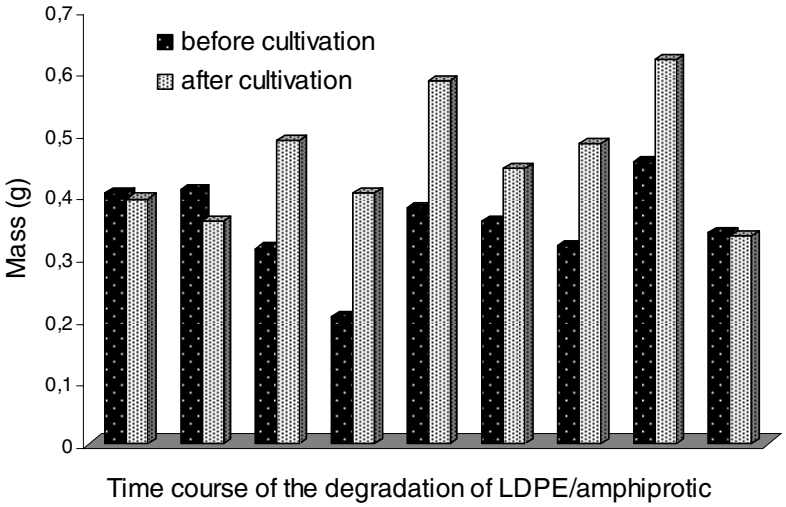

Figure 2. Representation of the LDPE/amphiprotic starch blend weight in function of the time course of the biodegradation.

Mechanical Tests

Initially, it was observed that the incorporation of starch to the polyethylene generated a new material that presented a special characteristic curve for tension versus specific deformation (Figure 3). As observed in Figure 3, the presence of the starch in the mixture promoted a decrease of the elongation capacity in relation to the pure polyethylene.

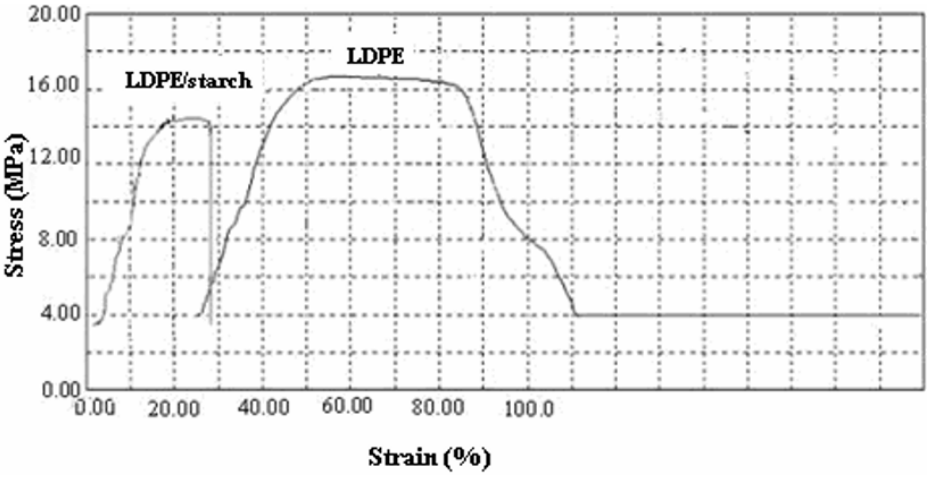

Figure 3. Stress (MPa) graph in function of the strain (%) for LDPE and LDPE/ starch blends.

A possible explanation for the change in the mechanical properties with the addition of starch to the polyethylene, could be a low interfacial interaction among the components of the blends, which may cause the mechanical rupture of their interface [19].

Rosa *et al*. [20] verified the influence on the mechanical properties due to the addition of starch to the polyethylene/starch blends. Changes were observed in the mechanical properties similar to the ones obtained in this work.

Arvanitoyannis *et al*. [18] showed that the greater percentage of starch in the LDPE/starch blend, the smaller its tensile strength and elongation at rupture. This change is accentuated when that percentage exceeds 20% starch.

Figures 4 and 5 show the growth of the fungi (biomass) in the biodegradation process in relation to tensile strength, and elongation at rupture (%El), respectively. It can be observed that the increase of the biomass production is related to the decrease of the mechanical properties. This fact can be attributed to the blend consumption, especially the consumption of the starch as a source of carbon for the fungi. This confirms the partial biodegradation of the polymeric blend.

It is likely that the gaps generated by the removal of the starch in the blend structure decreased the interfacial interaction even more. This is more evident in its elongation capacity as it presents greater sensitivity.

These results can be compared with Orhan & Büyükgüngör's [11] study of the degradation of LDPE/starch blends exposed to soil inoculated with the species *Phanerochaete chrysosporium*. The researchers proved the degradation of the blend by the reduction of the mechanical strength starting from day 30 of the test.

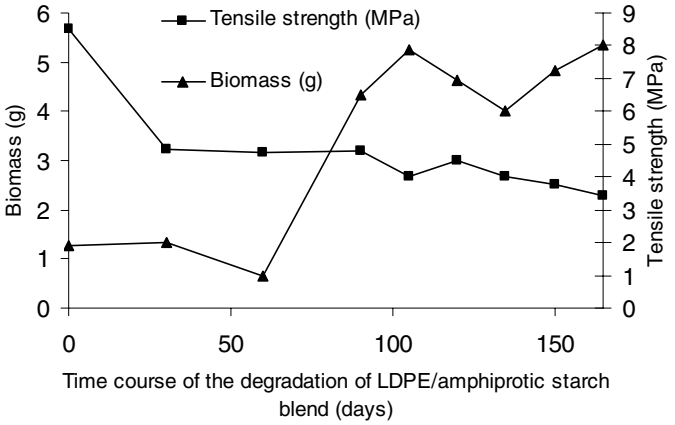

Figure 4. Tensile strength of the films when exposed to the fungi in the biodegradation test and biomass in function of the time course of the biodegradation of LDPE/amphiprotic starch blend.

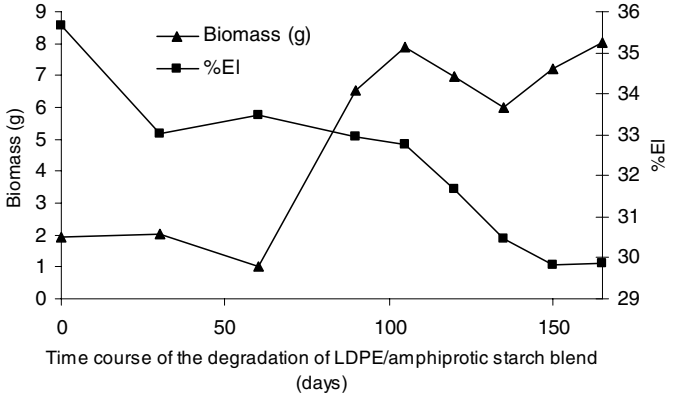

Figure 5. Elongation at break percentage (%El) when exposed to the fungi in the biodegradation test and biomass in function of the time course of the biodegradation of LDPE/amphiprotic starch blend.

Scanning Electron Microscope (SEM)

The micrographs presented in figure 6 show that the rupture of the samples not exposed to the fungi occurred in a more ductile way. This is evidenced by the formation of typical “fibers" of a material that presents a certain elongation before breaking when submitted to a force. It was noticed that with the increase of the polymeric blends exposure time, these "fibers" decreased, characterizing a less elastic material. Therefore, the material presented a smaller stretching capacity before rupturing, which shows that it became more brittle (Figure 7 and Figure 8).

Another characteristic that is also evident in the micrographs is the presence of starch in the interior of the polymeric matrix (Figure 6). Figure 7 also reinforces the theory that starch is the first to be consumed in the blend, since cavities are observed as a result of the starch consumption. Starch in the polymeric material also seems to be consumed when the time of blend exposure to the fungi is increased. As a result, the structure tends to reorganize to compensate for the cavities (Figure 8).

Kim *et al*. [21] verified the biodegradability of a blend of LDPE with potato starch using SEM. The destruction of the starch grains on the film surface by the bacteria *Pseudomonas aeruginos* was observed.

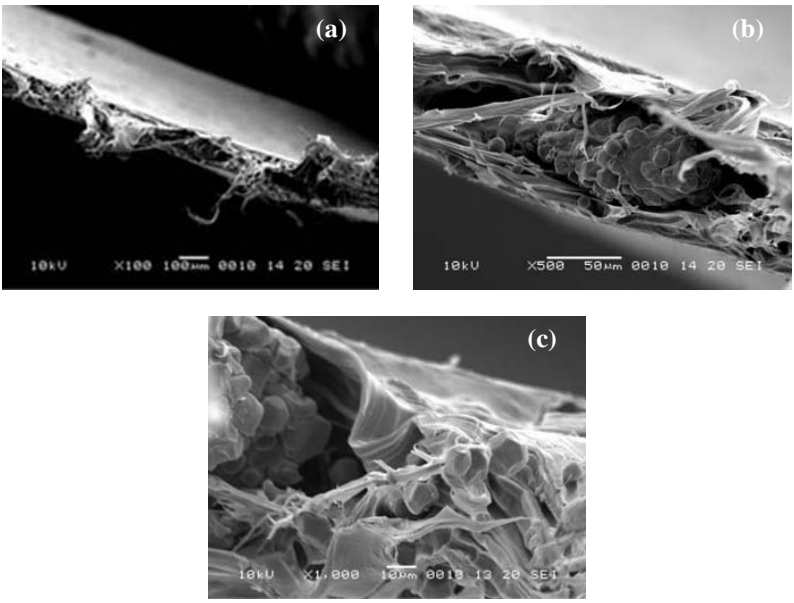

Figure 6. Micrographs of blends LDPE/amphiprotic starch without exposure to the fungi with increases of (a) 100x (—100µm), (b) 500x (—50µm) e (c) 1000x (—10µm).

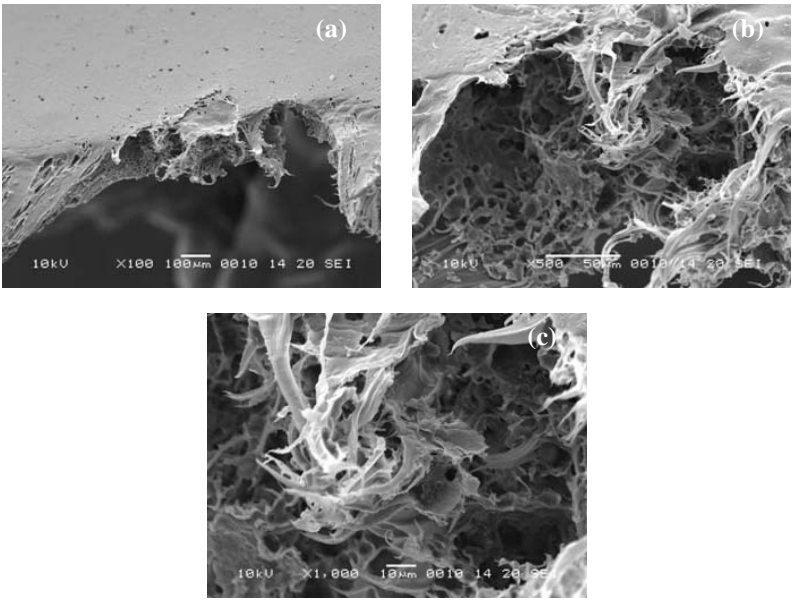

Figure 7. Micrographs of blends LDPE/amphiprotic starch with exposure of 90 days to the fungi with increases of (a) 100x (—100µm), (b) 500x (—50µm) e (c) 1000x (—10µm).

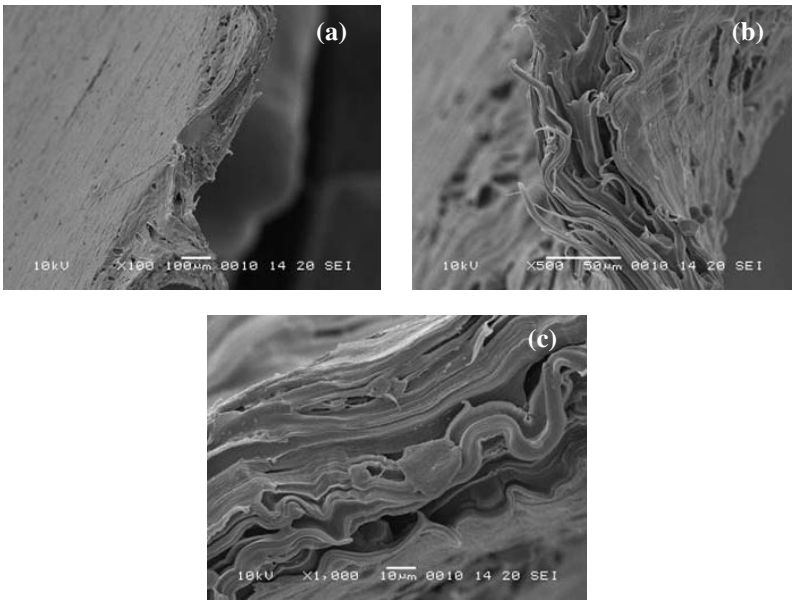

Figure 8. Micrographs of blends LDPE/amphiprotic starch with exposure of 165 days to the fungi with increases of (a) 100x (—100μm), (b) 500x (—50μm) e (c) 1000x (—10μm).

Sturm Test

Figure 9 presents the results of the daily CO_2 production with the CO_2 mass exclusion by culture medium (standard). It can be observed that there was a high production in the first days, followed by a random decrease, until it became stable. It is likely that this initial behavior is due to the consumption of the glucose present in the medium. It is believed that with the decrease of glucose in the medium due to the initial growth, the fungi started to consume the polymeric blends slowly, as an alternative source of carbon. The starch that was present in the blend is the most susceptible to enzymatic attack. This fact is easily explained by the facility of these fungi to produce amylases,

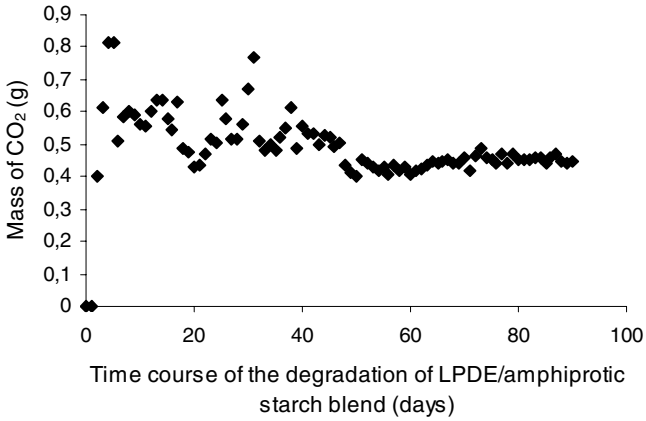

Figure 9. Production of CO_2 every day in function of the time of biodegradation of the polyethylene/amphiprotic starch under aeration, for the mixed culture.

which are enzymes that degrade starch, and also by the theory that the most amorphous area of the material structure is more accessible to attack by fungi [2].

Conclusions

The exposure of the polyethylene/starch blends to the fungi promoted an increase of the blends mass due to the impregnation of the *Phanerochaete chrysosporium* (Ph) and *Talaromyces wortmannii* (BM-10). The mass increase of the LDPE/amphiprotic starch blends is part of the biodegradation process. At this stage of the process, the microorganisms penetrate the polymeric matrix searching for nutrients that are scarce in the culture medium.

The fungi growth was observed during their exposure to the LDPE/amphiprotic starch blends which resulted in the loss of tensile strength and elongation at rupture of the polymeric material. This decrease in the mechanical properties was possibly caused by the starch consumption of the blend by the fungi. The fungi CO_2 production shows that starch can be consumed as a source of carbon. This carbon is then transformed into carbon dioxide and other by-products.

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