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ScienceDirect
Polymer Degradation and Stability 91 (2006) 3156–3162
Polymer Degradation and Stability
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# Degradation of sisal fibre/Mater Bi-Y biocomposites buried in soil

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Received 22 May 2006; received in revised form 21 June 2006; accepted 13 July 2006
Available online 25 September 2006

**Abstract**

Degradation of short sisal fibres/Mater Bi-Y™ biocomposites during indoor burial experiments was analysed. Within the first month, water sorption was the main event followed by weight loss. Water sorption results demonstrated that composites absorbed less water than the matrix. The lower sorption capacity of composites was related to the presence of fibre–fibre and fibre–matrix (both of carbohydrate nature) interactions which delay the water intake and enhances the material stability. In soil burial, all materials followed the same degradation pattern. The amorphous nature of the matrix favoured the preferential removal of starch, which was the most bio-susceptible material, as observed by thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). Fibres seemed to play a secondary role in this process, as confirmed by the slight difference in weight loss between the matrix and composites (40 and 33 wt.%, respectively). The drop in mechanical properties as a function of the exposure time was associated with the preferential loss of matrix and fibre components and the detriment of the fibre/matrix interface.


*Keywords:* Biocomposites; Biofibre; Biodegradation; Soil burial; Mechanical properties

## 1. Introduction

The growing problem related to finding available landfill areas for the final disposal of non-recyclable polymers gives rise to the development of biodegradable polymers and blends able to fulfil the new environmental requirements regarding the effective management of post-consumer waste [1,2]. Biodegradable polymers must be cost-effective and have to show similar performance to synthetic polymers. In order to achieve the above-mentioned characteristics, in recent years biodegradable polymers have been combined with natural fibres to produce environmentally sound biocomposites [3]. Scientific and industrial attention has been focused on the development of both, biodegradable polymers and their derived biocomposites. The current challenge is to design materials with structural and functional stability during storage and use, as well as susceptible to microbial degradation upon disposal with no adverse environmental impact [4,5].

Mater Bi-Y™ is a biodegradable material based on plasticized starch and cellulose derivatives [6,7]. This material is commercially available and shows similar properties as polystyrene. The addition of short sisal fibres was found to be cost-beneficial by decreasing the polymer volume fraction with additional improvement in some properties, such as thermal stability, creep behaviour and mechanical properties [8–10]. However, information about environmental biodegradability of Mater Bi-Y-based composites is still limited. Bastioli [7] reported that the presence of starch influences the biodegradation rate of the intrinsically biodegradable synthetic component during composting of Mater Bi-Y. On the other hand, the same material exposed to a respirometric test simulating soil burial conditions was only partially degraded up to about 18% [11]. The effect of natural fibres on the biodegradation of starch-based polymers and blends is still under study. Imam et al. [12] analysed the degradation of composites prepared from poly(vinyl alcohol), starch and orange fibres in soil. Results indicated that starch was the most bio-available

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doi:10.1016/j.polymdegradstab.2006.07.011

material and the presence of orange fibres did not greatly affect its degradation. On the other hand, short sisal fibres were reported to promote indirectly the biodegradation in biotic environments (soil and inoculated aqueous medium) of composites based on Mater Bi-Z™ [13]. Fibres appeared to be stable during the whole test (almost a year), but they may serve as a support for the microbial attack and favour the water entrance and the hydrolysis of starch, also associated with the presence of channels generated during the leaching of low molecular weight compounds. These results are in agreement with those reported by Modelli et al. [14] for the biodegradation of chemically modified flax fibres and starch powder in soil. Findings revealed that chemical modification did not strongly affect the total biodegradability of fibres and, on the other hand, half-life period for fibres was higher than that of starch. This effect must be considered when analysing the degradation in soil of starch-based biocomposites.

The present work is focused on the biodegradation of eco-friendly biocomposites based on cellulose derivatives/starch blends (Mater Bi-Y) and short sisal fibres buried in soil. Composition changes and mechanical behaviour of such materials exposed to natural microflora present in soil during indoor experiments were evaluated. Water sorption and weight loss as a function of degradation time were determined gravimetrically. The effect of biodegradation on the residual mechanical properties was also reported.

## 2. Experimental

Mater Bi-Y™, kindly supplied by Novamont (Novara S.P.A, Italy), was used as the matrix. The composition of this material was determined in previous work [12]: 38 wt.% of thermoplastic starch, 38 wt.% of cellulose derivatives and 22 wt.% of additives (i.e. natural plasticizers [6]). According to Bastioli [7], Mater Bi-Y is biodegradable and compostable material. Sisal fibres used as reinforcement were provided by Brascorda (Brazil).

Composites with 5–15 wt.% of sisal fibre were prepared in a Sandretto Serie Micro 30/107 injection machine and following the same procedure reported in a preceding paper [9]. Matrix and fibres were introduced into the injection machine without previous mixing, and rectangular plates of 19.7 cm × 9.8 cm × 0.3 cm were obtained. The average fibre length and diameter were measured before processing by means of an optical microscope. The average length was $7.2 \pm 0.6$ mm and the average fibre diameter was $0.3 \pm 0.05$ mm [9]. All samples were stored under vacuum and weighed before testing.

Dynamic thermal degradation experiments were carried out using a thermogravimetric analyser TGA-DTGA Shimadzu 50. Temperature was raised from 25 to 1000 °C, at a heating rate of 10 °C/min and under nitrogen (20 ml/min) in order to avoid thermo-oxidative degradation. The peak attribution was carried out according to the analysis reported in a previous paper [8].

Flexural tests were performed in a universal test machine (INSTRON 4467). The crosshead speed was chosen in accordance with ASTM D790M-93. All tests were carried out at room temperature.

The microstructure of the degraded samples was analysed by scanning electronic microscopy (SEM) by using a Phillips 505 electron microscope.

Indoor soil burial experiments were carried out as reported elsewhere [13]. Basically, a series of plastic boxes (30 cm × 15 cm × 10 cm) were used as soil containers. Natural microflora present in soil (Pinocha type) were used as degrading medium. Two specimens (rectangular shape, 60 mm × 13 mm × 3 mm), of Mater Bi-Y and each composite obtained from the same rectangular plate, were put into cups made of an aluminium mesh to permit the access of microorganisms and moisture and the easy retrieval of the degraded samples. The specimens into the holders were buried at a depth of 8 cm from the surface in order to ensure the aerobic degradation. The average room temperature was 20 °C and relative humidity was kept around 40% by adding distilled water.

Water sorption during soil burial was determined gravimetrically. Samples were removed from the soil at specific intervals ($t$), carefully cleansed with distilled water, superficially dried with a tissue paper and weighed ($w_h$). Water uptake ($\%WS$) was quantified by the following equation:

$$\%WS = \frac{w_h - w_t}{w_0} \times 100 \tag{1}$$

where $w_0$ is the initial mass, $w_t$ is the remaining mass due to biodegradation at time $= t$ and $w_h$ is the humid mass. The values reported are the average of two measurements.

After water sorption determination, samples were dried under vacuum and at room temperature to constant weight. The specimens were weighed on an analytical balance in order to determine the average weight loss ($\%WL$):

$$\%WL = \frac{w_0 - w_t}{w_0} \times 100 \tag{2}$$

where $w_0$ is the initial mass and $w_t$ is the remaining mass at time $= t$. All results are the average of two replicates.

## 3. Results and discussion

Mater Bi-Y and composites were exposed to natural microbial consortium during indoor soil experiments. Soil microflora constituted a mixed microbial population (including bacteria, actinomycetes and fungi) which may act synergistically during degradation and reproduce under naturally occurring conditions.

The experiment was carried out up to 400 days. After this time, samples could not be tested any more due to their macroscopic deterioration. It is important to point out that many potential errors may exist in gravimetrically measuring weight losses in soil, mainly at the later stages of the experiment. Soil, dirt and occluded biomass are difficult to remove without damaging the samples and may account for errors in determining the residual mass [13]. However, in spite of the above-mentioned drawbacks, weight loss data allowed us to evaluate qualitatively the effect of microbial attack on Mater Bi-Y and composites with short sisal fibres.

Water sorption and weight loss were evaluated on specimens recovered at predetermined time by retrieval of the aluminium containers. After recovery, samples were washed twice with distilled water, carefully dried and then weighed.

Fig. 1a and b summarizes the water sorption and weight loss for the neat matrix and composite with 15 wt.% sisal fibre. During the first 40 days both materials absorb enough water to ensure water bio-availability which favours the microbial attack and the hydrolysis of the matrix components. Within this period, both materials lost the same amount of mass (about 5%), but composites degraded faster than the neat matrix. Therefore, the presence of fibres seems to be relevant in promoting water intake and providing a rougher support for microbial growth [13,15,16]. Afterwards, water sorption rate decreased gradually and the unfilled matrix reached a pseudo-plateau well before the composite (75 vs. 320 days). The lower sorption capacity of composites may be related to the presence of fibre–fibre or fibre–matrix interactions which delay the water entrance [17–19]. On the other hand, weight loss was similar for both materials which allows us to assume that the most bio-susceptible material is one of the components of the matrix, starch or cellulose derivative.

In order to verify this assumption and evaluate the preferential attack on one of the components, the qualitative changes in the relative composition as a function of the degradation time were analysed by TG/DTG. Fig. 2a and b summarizes the changes of the relative composition during degradation for Mater Bi-Y and composite with 15 wt.% short sisal fibre. In a previous work, Alvarez and Vazquez assigned the different stages in TG curve to the degradation of each component in Mater Bi-Y and composites with short sisal fibres [8]. Before exposing to the degrading medium, the unfilled matrix shows two well defined peaks in the DTG curve (Fig. 2a): the first one was assigned to starch, meanwhile the second peak was attributed to the decomposition of cellulose derivatives. The first peak decreased gradually with the exposure time (with

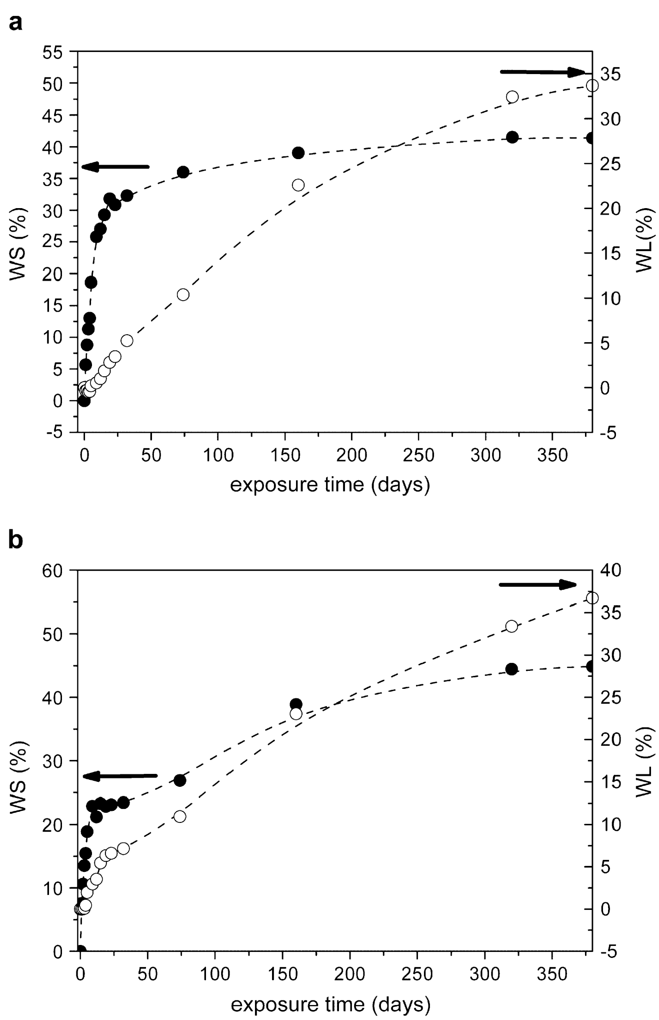


Fig. 1. Water uptake (●) and weight loss (○) as a function of exposure time in soil burial for (a) Mater Bi-Y and (b) composite with 15 wt.% of short sisal fibre.

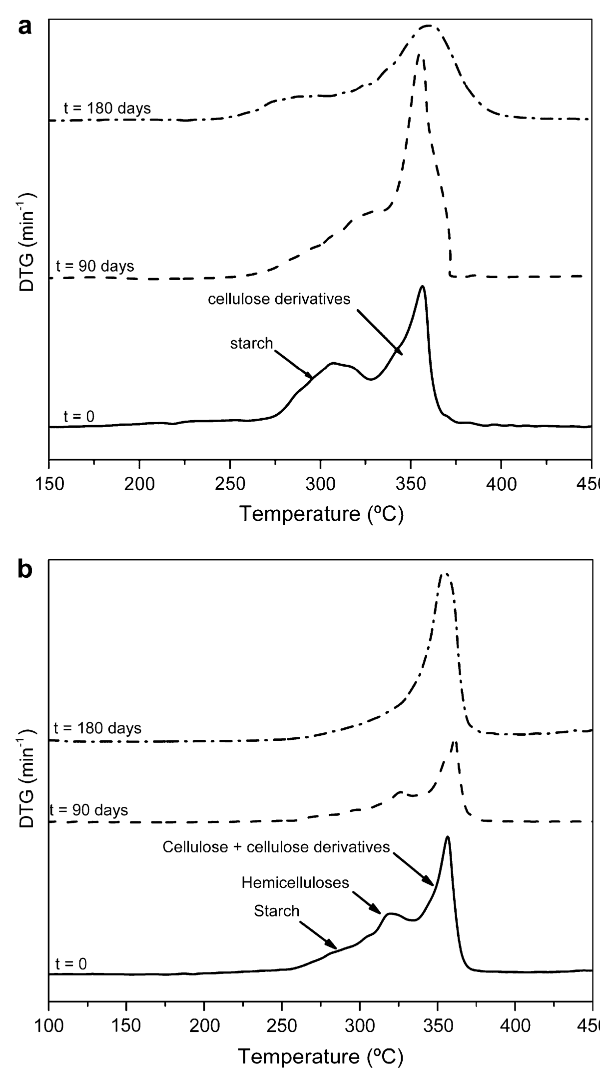


Fig. 2. Qualitative evolution of the relative composition of the exposed materials after different degradation times in soil burial determined from DTG curves. (a) Mater Bi-Y and (b) composite with 15 wt.% of short sisal fibre.

a relative increase of the second peak), being about 2% of the initial peak at the end of 180 days. This result is an indication that starch is the most bio-susceptible material of the matrix. On the other hand, the DTG curve for the composite (Fig. 2b) before soil burial showed two broad peaks which were assigned to the degradation of starch plus the contribution of hemicelluloses from the fibres, whereas the second one was attributed to the degradation of cellulose from the fibres plus cellulose derivatives from the matrix [8]. Cellulose and cellulose derivatives content was almost invariable, at least during the time length of the experiment, but changes in the relative content of starch and hemicelluloses were observed, as can be seen in Fig. 2b. In later stages of biodegradation, cellulose fibres may contribute to the slightly higher weight loss suffered by the composite. Microorganisms present in soil are relatively active to hemicelluloses at suitable humidity and temperature conditions [20]. The loss of starch, additives and hemicelluloses leads to highly brittle materials and is consistent with the macroscopic deterioration.

In order to visualize the morphological changes due to burial in soil, specimens of Mater Bi-Y and composite with 15 wt.% of short sisal fibre were collected at different degradation times and SEM micrographs were taken (Fig. 3a–f). At time zero the unfilled matrix exhibited a relatively smooth surface with some holes attributed to the processing (Fig. 3a). After 12 months, the erosion was clearly evident

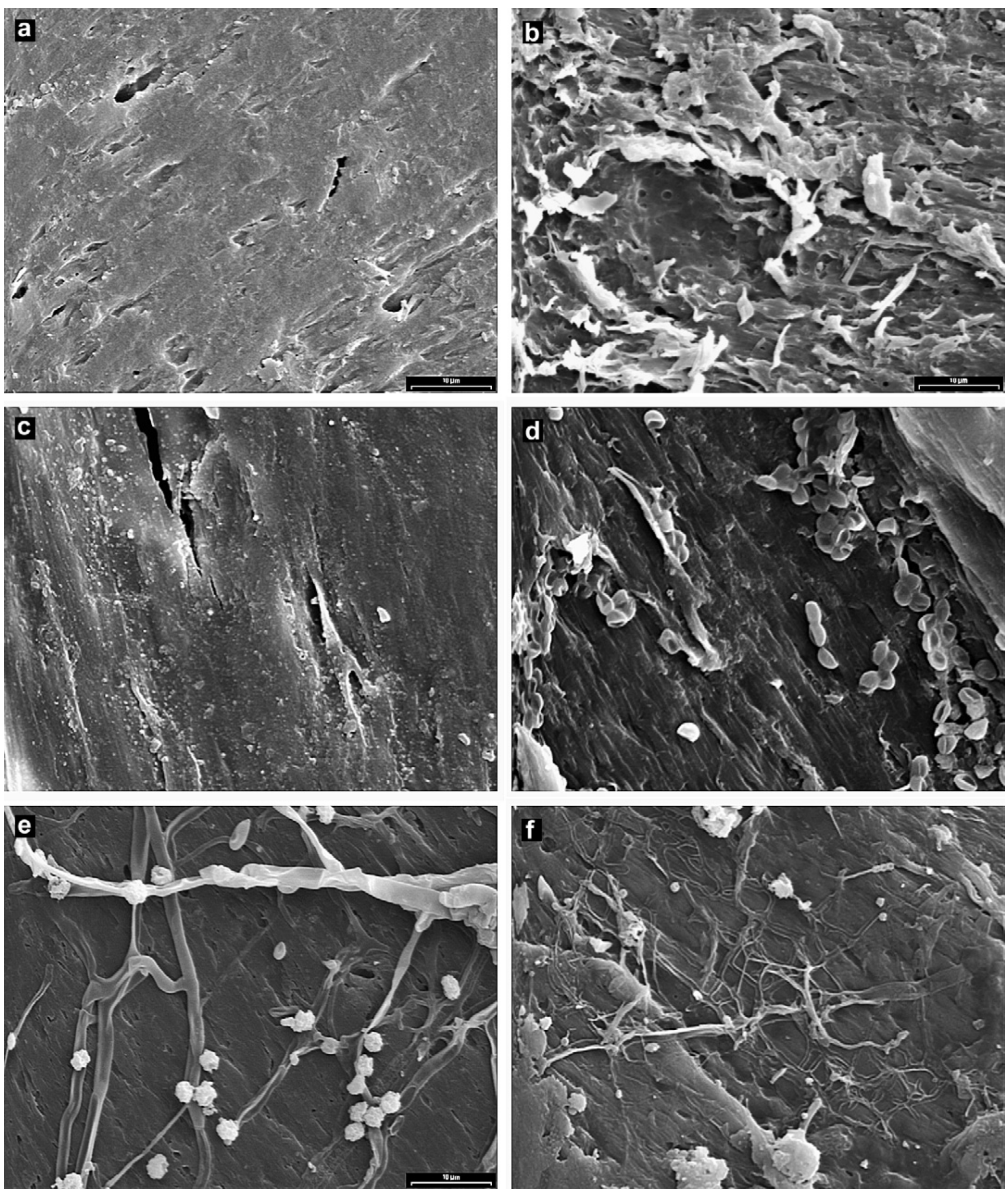


Fig. 3. SEM micrographs of the outer surfaces of samples after different exposition times to soil burial: (a) Mater Bi-Y before degradation; (b) Mater Bi-Y after 12 months; (c) composite with 15 wt.% of short sisal fibre before degradation; (d) composite with 15 wt.% of short sisal fibre after 12 months; (e) and (f) outer surface of Mater Bi-Y and composite with 15 wt.% of short sisal fibre specimen after 18 months of soil burial from which residues were not washed.

(Fig. 3b). The holes and cracks produced by biodegradation have random shapes, as usual in materials degraded in soils [21]. The delamination observed may be caused by the vacuum during sputtering of the sample for the SEM measurements. On the other hand, the composite with 15 wt.% short sisal fibre before exposure to soil, exhibited a smooth surface with similar irregularities to the neat matrix due to processing (Fig. 3c). After 12 months of soil incubation, SEM photographs revealed holes and cracks on the surface of the composite (Fig. 3d). Fibres also appeared more exposed due to the selective loss of starch from the matrix. SEM micrographs of the surface of the unfilled matrix and composite with 15 wt.% of filler recovered after 18 months after dirt cleaning, showed similar microbial attack (Fig. 3e and f). Both surfaces were colonized by filamentous microorganisms such as fungi and actinomycetes. These observations confirm that fibres have minor influence on the microbial attack in Mater Bi-Y composites.

The results obtained herein for Mater Bi-Y composites differ from those reported in our previous work for composites based on Mater Bi-Z (polycaprolactone/starch blend) where fibres were found to promote the biodegradation and then, the preferential removal of starch [13]. Mater Bi-Z is a semicrystalline blend (m.p. = 60 °C), whereas Mater Bi-Y is amorphous. Crystalline regions are more difficult to degrade and may act as preference points for the microorganisms intake. Fibres may act as channels and facilitate the microbial attack in natural fibre–semicrystalline matrix composites. In the case of Mater Bi-Y, the amorphous structure favours the microbial accessibility to the matrix (mainly to the destructured starch) and fibres have a minor role, as can be concluded from the slight difference in weight loss suffered by the matrix and the composites (see Fig. 1).

Materials deterioration and weight loss were accompanied by loss in their mechanical properties. The residual mechanical properties were also evaluated by the following relationship:

$$\left(\frac{P}{P_0} \times 100\right) \tag{3}$$

where $P$ is the selected property measured at a time of exposure $t$ and $P_0$ is the initial property. The obtained results of flexural tests for the unfilled matrix and composites at different incubation times are summarized in Fig. 4. Initially, composites exhibited higher values of flexural modulus, 2.8 GPa for the unfilled matrix and 3.15 GPa for the 15 wt.% sisal fibre composite. After 12 months of soil burial, flexural modulus decreased drastically for both materials, being more significant for the composites and consistent with the weight loss results. For the unfilled matrix, this behaviour may be attributed to the preferential loss of starch, whereas in the case of composites this effect is combined with the fibre/matrix interface detriment. Fibre debonding and matrix degradation conduct to a lower adhesion at the interface and, consequently, to poorer mechanical properties. Samples incubated for 18 months could not be tested because of the deterioration of the materials due to significant colonization (see Fig. 3e and f).

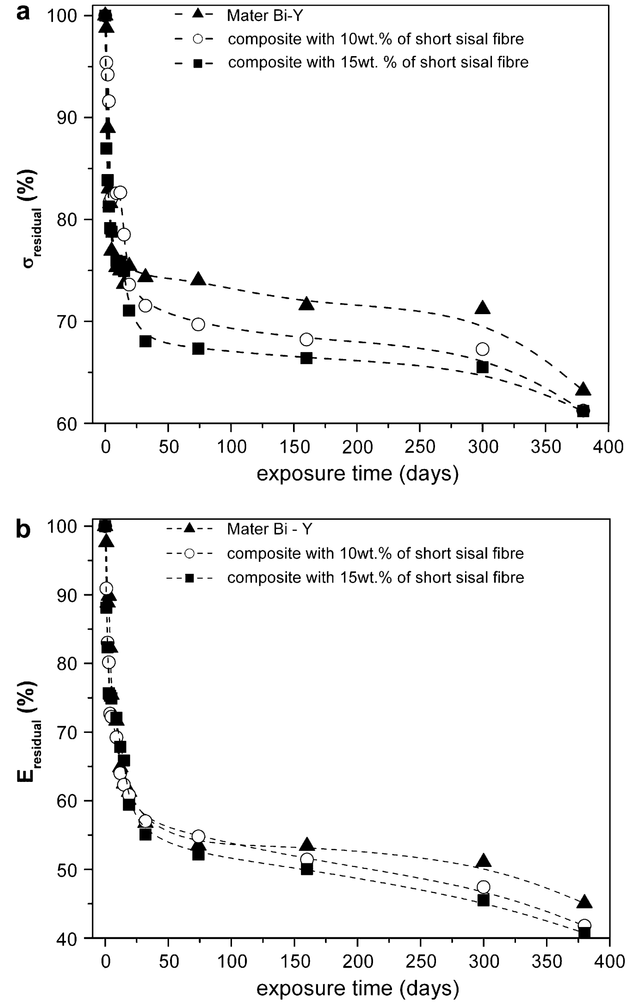


Fig. 4. Residual mechanical properties as a function of the degradation time. (a) Flexural strength and (b) flexural modulus.

Electron micrographs of the fracture surface of Mater Bi-Y and composite with 15 wt.% of short sisal fibre before and after 15 months of soil burial are shown in Fig. 5. Undegraded samples are characterized by a continuous and smoother fracture surface (Fig. 5a and b), whereas degraded ones (Fig. 5c and d) show irregularities and fibres are still visible in the composites. Indeed, holes are clearly visible on degraded samples of both materials and it is an evidence that starch is preferentially removed during soil exposition.

## 4. Conclusions

Degradation during indoor soil burial experiments of cellulose derivatives/starch blends and their composites with short sisal fibres was analysed. Mixed undefined microbial population present in the soil microflora was used as degrading medium as it can be considered a realistic approach to the biodegradation process in natural environments. According to the results, it is shown that Mater Bi-Y and its

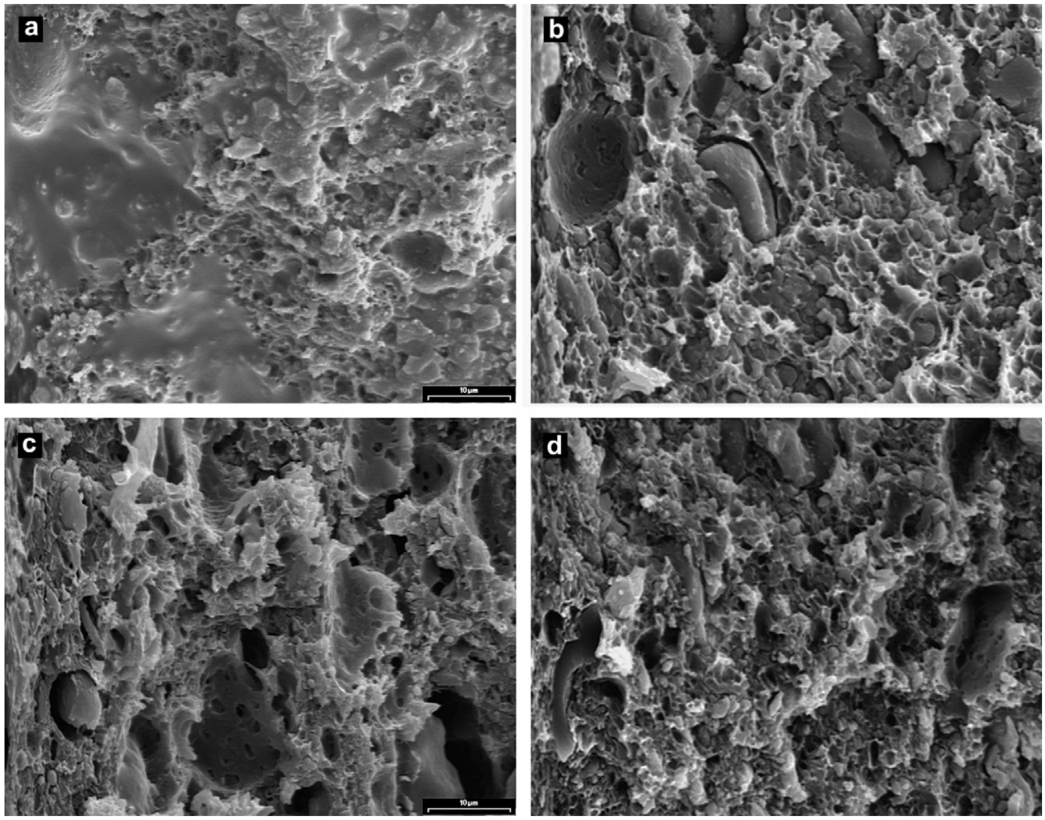

Fig. 5. SEM micrographs of the fracture surface after flexural tests. (a) Mater Bi-Y before degradation; (b) Mater Bi-Y after 15 months of degradation in soil; (c) composite with 15 wt.% of short sisal fibre before degradation; (d) composite with 15 wt.% of short sisal fibres after 15 months of degradation in soil.

composites are potentially degradable in natural environment or landfills.

As a general trend, water sorption prevailed over the weight loss within the first month of the experiment for both materials. Composites showed an unexpected improvement in water resistance. This behaviour was related to the less hydrophilic character of cellulose fibres in comparison to starch and to the fibre–fibre and fibre–matrix interactions.

Within the first 75 days, the water intake promotes the entrance of microorganisms present in soil due to the higher water availability within the material, and then biodegradation begins. Results revealed that during the first month, the matrix and composites lost around 5% of their initial mass, due to the leaching of low molecular weight compounds, such as additives. From this point until the end of the experiment, both materials showed a sustained weight loss. The amorphous nature of the matrix could be considered as the main responsible of the similar degradation pattern obtained for all the materials tested. The slightly higher weight loss suffered by the composites may be due to the presence of fibres which play a secondary role acting as a support for microbial growth.

The mass loss was accompanied by a considerable decrease in mechanical properties, which is an indication that both materials are fairly sensitive to microbial degradation in soil. Fracture surfaces after 15 months of treatment appeared more heterogeneous and showed holes attributed to the preferential removal of one of the components of the matrix. Indeed, TG/DTG measurements performed on degraded samples evidenced the preferential sensitivity of starch to the degrading medium.

The results obtained herein clearly demonstrate that Mater Bi-Y and composites with short sisal fibres show limited lifetime in biotic environment which make them suitable for being disposed in landfills after their use.

## Acknowledgements

The authors acknowledge to CONICET and SECYT (PICT 12-15074) for their financial support.

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