

Degradation of polycaprolactone/starch blends and composites with sisal fibre

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Abstract

The susceptibility of polycaprolactone/starch (PCL/S) and sisal fibre-reinforced polycaprolactone/starch blends (SF-PCL/S) to different degrading environments was evaluated. The composites and the unfilled matrix showed hydrolytic stability at pH 7.2 at two different temperatures (25 °C and 40 °C). Fibres were stable under hydrolytic conditions and seemed to favour the entrance of water and then, the swelling and the hydrolysis of the starch (the most bio-available component). At higher fibre content, the composites become more hydrolytically stable probably due to the presence of a fibre–fibre physical network. Microbial attack in biotic aqueous medium was evidenced by the presence of a biofilm, especially on the fibre surface. In soil burial, PCL/S and 15%SF–PCL/S were degraded to about 50% of the initial mass. The weight loss pattern showed by the composite was associated with the presence of strong fibre–fibre and fibre–matrix interactions, which are absent in the neat matrix.

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1. Introduction

In the last decades, biodegradable polymers and blends have been developed as a response to the public environmental concern caused by the growing problem of plastic waste [1]. Besides solutions such as recycling, re-use and combustion with energy recovery, biodegradable polymers can be entirely converted by microbial activity in a biologically active environment to biomass and biological by-products. This process can be considered as a biologically mediated recycling of plastic items [2].

Among all biodegradable polymeric materials that are nowadays commercially available, blends based on destructured starch and hydrophobic synthetic polymers, such as aliphatic polyesters, have received increasing industrial attention for using as commodity

plastics [3,4]. One of these materials, which are on the market as Mater BI™ (Z class, Novamont, Novara S.p.A, Italy), is characterized by good mechanical properties, low sensitivity to water, biodegradability, compostability, compatibility with different waste disposal and wide range of processing grades [3,5–7]. However, the current price of such materials is their major drawback for using them in large-scale applications. An eco-friendly alternative to overcome this limitation with the additional advantage of improving physical and mechanical properties, is to incorporate bio-fibres (natural fibres) into biodegradable matrices in order to obtain biocomposites, which are quite similar to the already known synthetic fibre–reinforced–polymers [8,9].

Several studies have been carried out to evaluate the degradation and biodegradation of PCL/S blends. Bastioli et al. [3,5–7] reported the degradation of Mater Bi in composting environment. These authors claimed that the presence of starch can influence the biodegradation rate of the intrinsically biodegradable synthetic component. Avella et al. [10] found that the incorporation of a compatibilising agent into PCL/S blend

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improved the biodegradability of PCL during composting. Recently, Singh et al. [11] analysed the biodegradation of PCL/S in composting and culture environments. The results revealed that granular starch enhances biodegradation in comparison with PCL-waxy starch. Similar results were reported by Ishiaku et al. [12], for the enzymatic hydrolysis of PCL/S blends. Glucamylase selectively hydrolyses the starch of the composite and granular sago starch undergoes higher weight loss than thermoplastic. This behaviour may be attributed to the higher surface area exposed to enzyme activity. So, destructuring the starch reduces biodegradability. Solaro et al. [13] described a respirometric test simulating soil burial conditions for a variety of biodegradable materials. Mater Bi was only partially degraded up to about 18% of the theoretical carbon dioxide and reached a plateau after 120 days. Rutkowska et al. [14] reported the degradation of PCL/S blends in different natural environments, such as Baltic Sea water, compost with active sludge at sewage farm and in the laboratory. The results in natural sea water showed that samples were destroyed after 4 weeks due to the microbial activity, salt and sunlight. However, in spite of the above-mentioned studies, there is a lack of information about the biodegradation and the hydrolytic stability of PCL/S blends reinforced with natural fibres.

In the field of biocomposites, Vázquez and co-workers have been working on the development of sisal fibre–polycaprolactone/starch composites (SF–PCL/S). Thermal and physical properties, processing conditions, isothermal and non-isothermal crystallization, thermal degradation and mechanical properties have been extensively studied [15–19]. The aim of the present work is to analyse the susceptibility of such materials to hydrolytic and microbiologically influenced degradation, under different degrading conditions. Weight loss is measured gravimetrically as a function of the degradation time. Changes in the relative composition after exposure to degradation conditions are evaluated by thermogravimetric analysis (TGA). Morphological changes are analysed by scanning electron microscopy (SEM) and optical microscopy (OM).

2. Experimental

2.1. Composite preparation

A commercial polymeric material based on starch (S), polycaprolactone (PCL) and natural additives, was supplied by Novamont (Novara S.p.A, Italy) [3]. Sisal fibre, used as reinforcing material, was purchased by Brascorda (Brazil).

The composites with different weight content of sisal fibre (SF–PCL/S) were prepared as reported elsewhere [15]. SF–PCL/S pellets were transformed into

rectangular plates (19.7 cm × 9.8 cm × 0.3 cm), in an injection machine model Sandretto-Serie Micro 30/107. The average diameter (D) and length (L) of the fibres was determined by optical microscopy on fibres solvent-extracted from the matrix [15]. The diameter was 0.15 ± 0.07 mm and the final length was 2.6 ± 0.6 mm. The average length/diameter ratio (L/D) was 17.3. The rectangular plates were cut into discs of 10 mm of diameter and 3 mm thickness. The specimens were carefully dried under vacuum and weighed before testing.

2.2. Degradation experiments

2.2.1. Indoor soil burial

The experiment was carried out in a series of plastic boxes (30 cm × 15 cm × 10 cm) containing characterized soil (Pinocha type) and the natural microflora present was used. Two specimens (disk shape, 10 mm of diameter and 3 mm of thickness), of PCL/S and SF–PCL/S of each composition and obtained from the same rectangular plate, were tested. The samples were put into containers (cup shape) made of stainless-steel mesh. These holders permit access of microorganisms and moisture, and can be easily pulled out for the retrieval of the degraded samples. The cups were buried at a depth of 8 cm from the surface. The relative humidity was kept around 40% and the temperature was 20 °C. At predetermined intervals, the specimens were removed from the soil, carefully cleansed with deionized water and finally dried under vacuum to constant weight. The samples were weighed in order to determine the weight loss by Eq. (1):

$$\text{WL}\% = [(m_0 - m_t)/m_0] \times 100 \quad (1)$$

where m_0 is the initial mass, m_t is the final mass (after dried) at a predetermined time t . An average of two measurements was taken.

2.2.2. Hydrolysis

The specimens of PCL/S and SF–PCL/S were immersed in 30 ml of phosphate buffer pH 7.2, and kept sterile by adding 0.02% (w/v) of NaN_3 . Incubation took place at two different temperatures, 25 °C and 40 °C. Samples were removed at specific intervals, cleaned and dried under vacuum to constant weight. Weight loss was determined by Eq. (1).

2.2.3. Pure cultures of amylolytic–cellulolytic bacteria

Several bacterial strains were isolated from soil by enrichment on minimal salt media using two different sources of carbon: 0.1% starch and 0.1% microcrystalline cellulose. From the 12 bacterial strains isolated, only those showing the higher rate of growth on starch were selected for the degradation experiments. Samples of materials were sterilized (alcohol 70%, UV), and

immersed in culture flask containing 25 ml of minimal salt media. Cultures were inoculated by addition of 25 ml of a bacterial pre-culture grown on the same mineral media to which starch was added. Batch incubations were developed at room temperature and were under continuous shaking for 2 months.

At selected times, samples were recovered, observed in the optical microscope and dried to constant weight under vacuum. Sterile controls were run in analogous conditions.

2.3. Methods of analysis

Dynamic degradation measurements were carried out using a thermo-balance SII Exstar 6000 Seiko Instruments, operating from 30 to 600 °C, at a heating rate of 10 °C/min and under nitrogen (20 ml/min) in order to avoid thermo-oxidative degradation.

The surface changes were examined by dark field optical microscopy (OM) by using an Olympus PMG3 Metallurgical microscope at 50× magnification.

Scanning electron micrographs were taken on gold-coated surface of the specimens after degradation, by using a Phillips 505 electronic microscope.

3. Results and discussion

3.1. Initial composition of the samples

Thermogravimetric analysis was used as a tool to determine the relative composition of the samples before testing. The TG/DTG curves of PCL/S and 15%SF–PCL/S before exposing to different degradation environments are shown in Fig. 1(a) and (b), respectively. DTG curve for the unfilled matrix (PCL/S) shows three peaks, corresponding to the three steps in TG curve. The first peak at 225 °C, is attributed to the maximum degradation rate (T_{\max}), due to the loss of low weight compounds such as natural additives. The second and third peaks were attributed to starch ($T_{\max} = 322$ °C), and PCL ($T_{\max} = 408$ °C), respectively, by comparing with the values reported for the pure components determined in the same conditions [16]. The peaks for the composite were evaluated taking into account the presence of sisal fibre which presents two peaks in DTG curves: hemicellulose, at $T_{\max} = 289$ °C, and the major component, cellulose at $T_{\max} = 352$ °C. The peak corresponding to lignin is completely overlapped by the other peaks [20]. The DTG curve of 15%SF–PCL/S (Fig. 1(b)), shows at least four peaks. A large first peak (191–230 °C), is attributed to the loss of low molecular weight components; the second peak ($T_{\max} = 311$ °C), may be assigned to starch plus the contribution by overlapping, of the first peak of the sisal

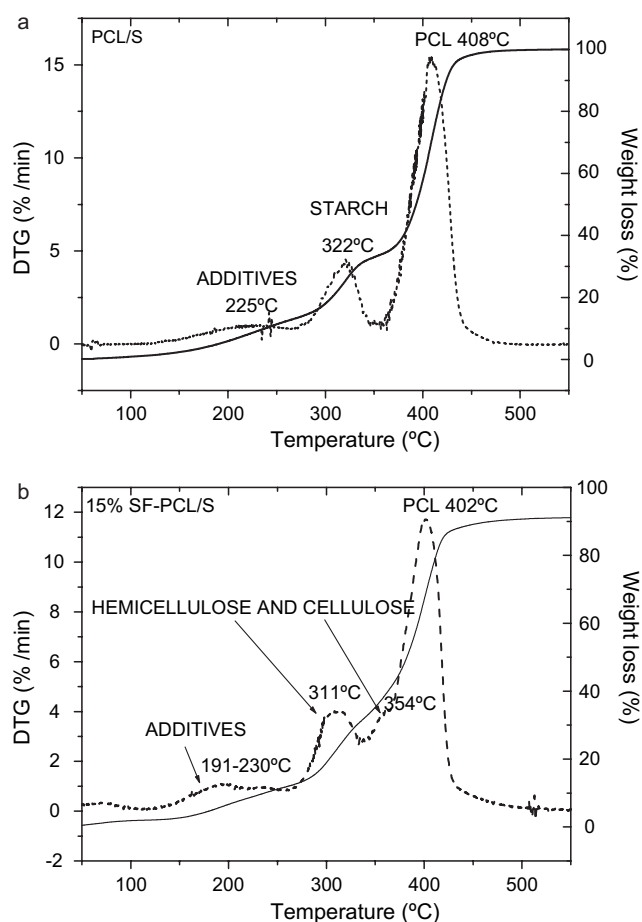


Fig. 1. TG/DTG curve obtained at 10 °C/min under nitrogen atmosphere before exposure to degradation environments: (a) PCL/S; (b) 15%SF–PCL/S.

fibre (hemicellulose); the shoulder at $T_{\max} = 354$ °C is attributed to the second peak of sisal fibre (attributed to cellulose) and the fourth and main peak represents the degradation of PCL.

The amount of weight loss in TG process is equal to the integral of the DTG curve against temperature. The area under each peak represents the weight loss of each component. However, it is evident that there is an overlap of peaks (particularly in the case of the composite), which is the main problem for quantitative analysis in TG experiments. In this work, a deconvolution method was used as a first approach for splitting the peaks and evaluating the relative contribution of each component. However, for the composite, the method was not able to split the shoulder into peaks. As a result, starch content was bigger than expected due to the contribution of the hemicellulose peak, and PCL content was lower due to the overlapping with cellulose peak. At this point, it is important to remark that the relative composition calculated herein will be only used as a parameter to estimate the degree of degradation and the susceptibility of the different components of the

Table 1
Initial relative composition for PCL/S and 15%SF–PCL/S evaluated from TG/DTG experiments

	Initial contents (%)	
	PCL/S	15%SF–PCL/S
Additives	9	8
Starch	16	25 ^a
PCL	75	45
Cellulose	–	21

^a Starch + hemicellulose.

blends to the degradation media. Table 1 summarizes the initial content of each co-component for PCL/S and 15%SF–PCL/S.

3.2. PCL/S and 15%SF–PCL/S in soil burial

Degradation of PCL/S and 15%SF–PCL/S samples was evaluated by indoor soil burial experiments for 9 months. Samples were removed at predetermined times, cleansed before dried and weighed. It is important to remark that weight loss measurement is not the best strategy for evaluating degradation in soil, mainly in the later stages of degradation. Many potential errors exist in measuring degradation rate by weight loss. Soil occluded inside the samples is difficult to extract without damaging the samples. Also, bacteria and dirt not removed during washing may account in errors in determining the residual mass [21]. However, the analysis of weight loss data allowed us to evaluate the influence of the presence of sisal fibre during degradation in soil.

Fig. 2 represents the average weight loss (two specimens) determined by applying Eq. (1), for both materials. During the first month, the unfilled matrix and the composite with 15% in weight of sisal fibre show a similar weight loss. This behaviour may be associated

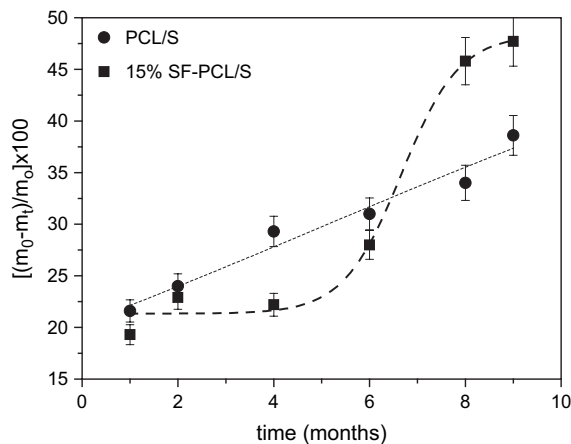


Fig. 2. Weight loss as a function of degradation time during soil burial: (a) PCL/S; (b) 15%SF–PCL/S.

to the loss of low molecular weight compounds such as additives, as was confirmed by TG analysis. During all the times of the experiment, the PCL/S showed a constant weight loss, meanwhile the composite showed different stages. During the first step, 15%SF–PCL/S presents a burst and no further weight loss was observed until the third month. During this period and in the absence of additives, strong fibre interactions, due to H-bonds, may produce a physical network which prevents the water uptake, and thus reduces the accessibility to soil microflora. These kind of interactions between cellulose fibres has been proposed by Dufresene et al. [22,23], for systems composed by thermoplastic starch and microfibrils obtained from potato pulp. The same authors claim that the presence of additives such as polyols prevents the formation of this network [23]. After the sixth month, the weight loss of the composites increases rapidly until reaching a remaining mass of about 50% of the initial one. This increment may be related to two factors: the leaching of starch (the more biosusceptible material) produces channels which favour the entrance of water and microorganisms present in soil, and then the biodegradation rate increases. Second, the presence of a consortium of bacteria and fungi at the later stages of the biodegradation can act in a synergetic way and the degradation process can be promoted.

In order to evaluate the preferential attack on one of the components, the changes in the relative composition as a function of the degradation time was analysed by TG/DTG. Fig. 3(a) and (b) shows the evolution of the relative composition during degradation of PCL/S and 15%SF–PCL/S, respectively. The starch peak decreases gradually (with a relative increment of the peak of PCL). This last result confirms that starch is the most biosusceptible component of the blend. For both systems, additives and low molecular weight components decrease to zero during the first month. Starch composition decreases gradually, being about 7% at the end of the sixth month; meanwhile PCL content was almost invariable at least during the time of the experiment. For the composite, the PCL content was also invariable, but changes in the relative content of starch and cellulose were observed, as can be seen in Fig. 3(b). Even if sisal fibres are stable during matrix degradation, it is well reported that natural fibres are degraded biologically because of the microorganisms present in soil attack, which are relatively active to hemicelluloses under suitable temperature and humidity conditions [1,24]. In later stages, cellulose chain breakdown may contribute to the higher weight loss suffered by the composite.

The above-mentioned results agree with SEM observations. Fig. 4(a)–(e) shows SEM analysis of PCL/S and 15%SF–PCL/S surfaces before and after 9 months of exposure to soil burial. PCL/S shows a smooth surface before degradation (Fig. 4(a)). After 9 months, PCL/S displays an irregular surface with channels, as

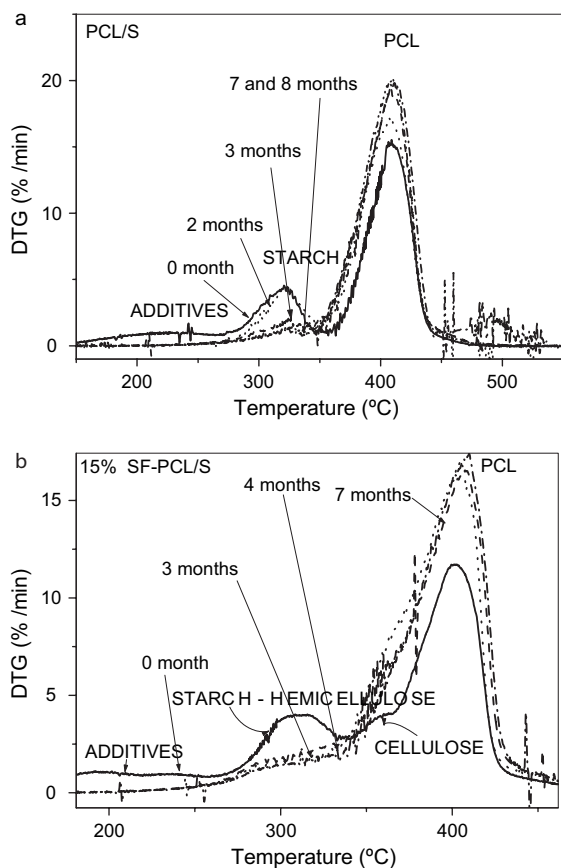


Fig. 3. DTG curves obtained after different degradation times in soil burial: (a) PCL/S; (b) 15%SF-PCL/S.

a consequence of the preferential removal of the starch Fig. 4(b)). On the other hand, the SEM analysis on the composite surface shows that sisal fibres are still visible, even after 9 months (Fig. 4(d)). This result indicates that the fibre surface promotes the water entrance and the swelling of the starch component and serves as a support for the attack of microorganisms. The preferential attack throughout sisal fibre was confirmed, from comparing SEM micrographs of PCL/S and 15%SF-PCL/S after 9 months in soil burial from which just the dirt was cleaned: only specimens containing sisal fibre showed microorganisms (bacteria) attached in the cavities near the fibre surface in which degradation proceeds (Fig. 4(e)). So, sisal fibres seem to promote indirectly biodegradation of PCL/S. Similar results were reported by Nitz et al. [25], for composites based on PCL and wood flour (WF).

3.3. Chemical hydrolysis of PCL/S and SF-PCL/S

The neat PCL/S and the composites with different fibre content (from 5 to 15% in weight) were immersed in phosphate buffer pH 7.2 and in the absence of micro-

organisms for almost one year. Under the conditions of the experiment, PCL and sisal fibres are reported to be stable [7,24]. Thus, the main reaction expected should be the hydrolysis of the starch.

PCL/S and SF-PCL/S showed hydrolytic stability, at least for one year. PCL/S absorbed around 21.5% water. The presence of fibres slightly increases the swelling of the material, i.e. 22.5% for 15%SF-PCL/S [16].

The weight loss curves for PCL/S and the composites with different fibre content are shown in Fig. 5. Weight loss is related to the diffusion of low molecular weight compounds, such as additives and degradation products, to the aging medium. During the first month, all the samples lost almost the same weight, mainly due to the diffusion of low molecular weight additives. DTG analysis confirmed this result, as in the case of soil burial. As the degradation proceeds, the composite with 5% of fibre content in weight suffers slightly higher weight loss as can be seen in Fig. 5. Cellulose fibres can act as channels to promote the water diffusion into the compound and then, the hydrolysis of the matrix. The same results have been reported for composites based on polycaprolactone and wood flour [25]. However, as the fibre content increases, the composites suffer an unexpected improvement in water resistance. This behaviour may be associated with the less hydrophilic character of the cellulose fibres in comparison to starch [21]. Besides, at a higher fibre content (> 5%), strong fibre–fibre and fibre–matrix interactions may be present, which prevent the water intake and, as a consequence, the swelling of the starch [21,22]. As it was mentioned above, additives were lost during the first month, then the presence of a physical network between the carbohydrates is highly probable.

Fig. 6(a) and (b) shows the DTG curves as a function of the degradation time for PCL/S and 15%SF-PCL/S, respectively. As the degradation proceeds, the starch peak in PCL/S suffers a slight decrease and a widening. Water produces the starch chain scission; however, the chain fragments are not small enough to diffuse to the aging media. The widening in DTG peak could be associated to a widening in the molecular weight distribution of starch [16]. On the other hand, PCL seems to be stable. After one year, PCL peak shows a relative increment as a consequence of the loss of the additives and a low molecular weight—starch degradation products. Additives and starch final weight loss were 100% and 11%, respectively. On the other hand, the evaluation of the changes in composition for the composites was rather difficult because of the overlapping between the starch and the sisal fibre (Fig. 6(b)). However, as in the case of PCL/S, PCL seems to be invariable during the time of the experiment.

Fig. 7 shows a scanning electron micrograph of the surface of a PCL/S blend after 6 months of aging in buffer solution. The surface seems to be eroded, however

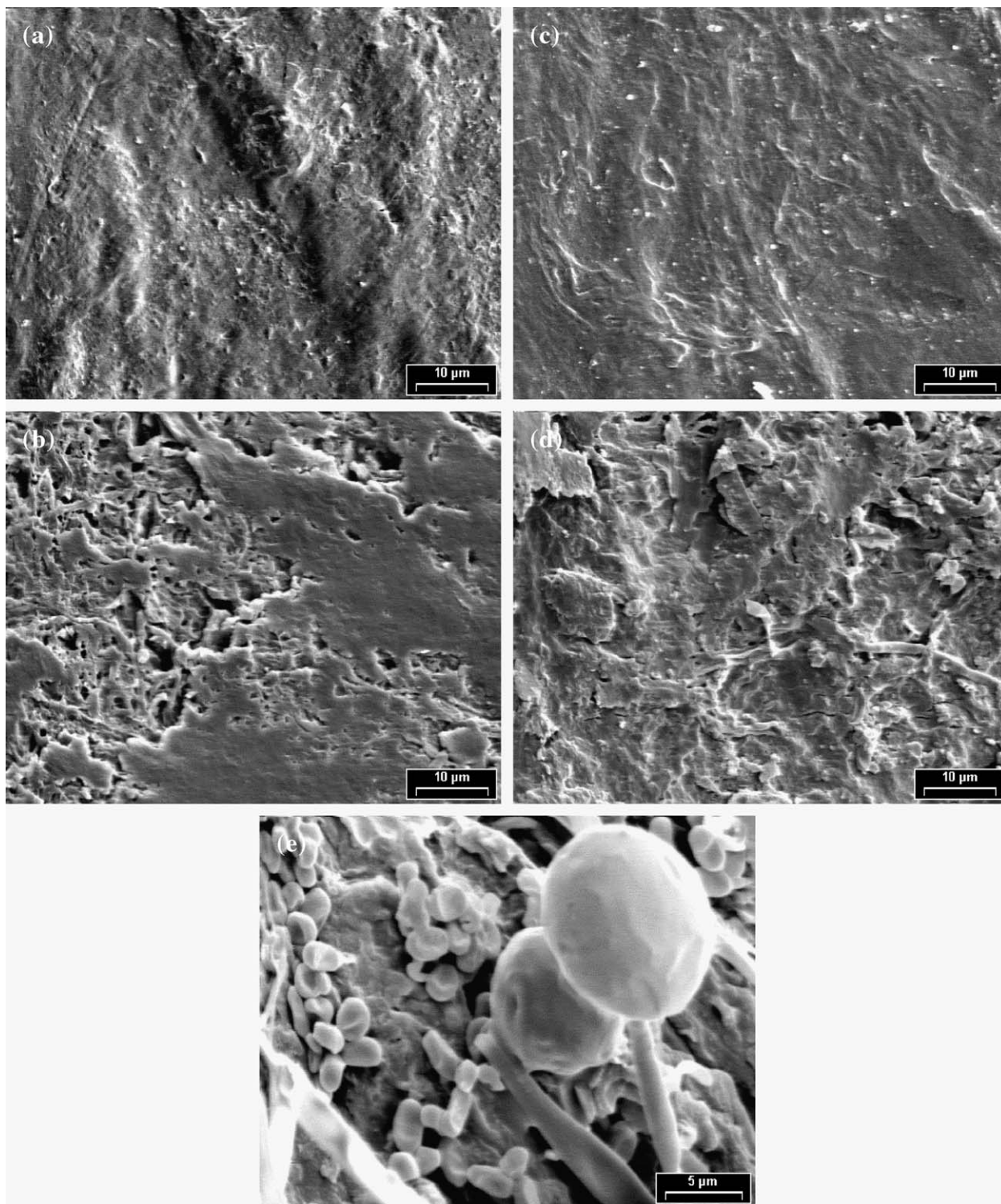


Fig. 4. SEM micrographs of the surfaces of the samples: (a) PCL/S before biodegradation; (b) PCL/S after 9 months of soil burial; (c) 15%SF–PCL/S before biodegradation, (d) 15%SF–PCL/S after 9 months; (e) outer edge of a 15%SF–PCL/S specimen after 9 months of soil burial from which residues were not washed.

the weight loss remains low. The same effect was observed for the composites. This effect on the surface may be caused by the vacuum during sputtering of the sample for the SEM experiments.

Hydrolytic degradation was also evaluated at 40 °C. An increase in the degradation temperature may produce an increase in the accessibility of water molecules. In agreement with the last assumption, a higher

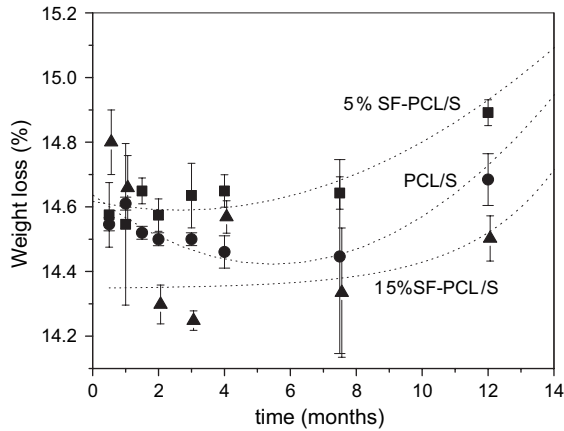


Fig. 5. Weight loss curves determined during hydrolytic degradation of PCL/S, 5%SF-PCL/S and 15%SF-PCL/S.

hydrolytic degradation was observed due to the higher chain mobility at 40 °C. This experiment allowed us to find a temperature–time correlation between both essays. Indeed, 5 months at 40 °C produced the same weight loss than 12 months at 25 °C.

The water stability showed by PCL/S can be mainly attributed to PCL. The hydrophobic character of PCL

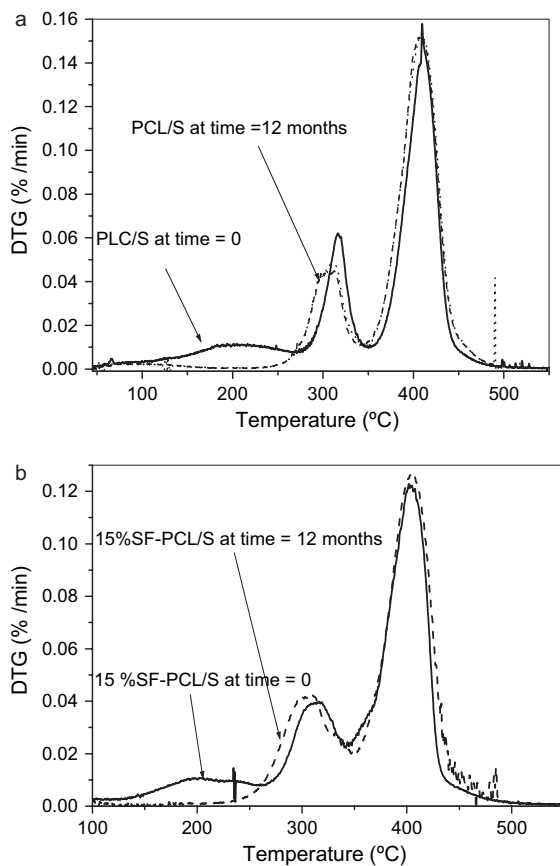


Fig. 6. DTG curves of the specimens after 12 months of aging at pH 7.2: (a) PCL/S, (b) 15%SF-PCL/S.

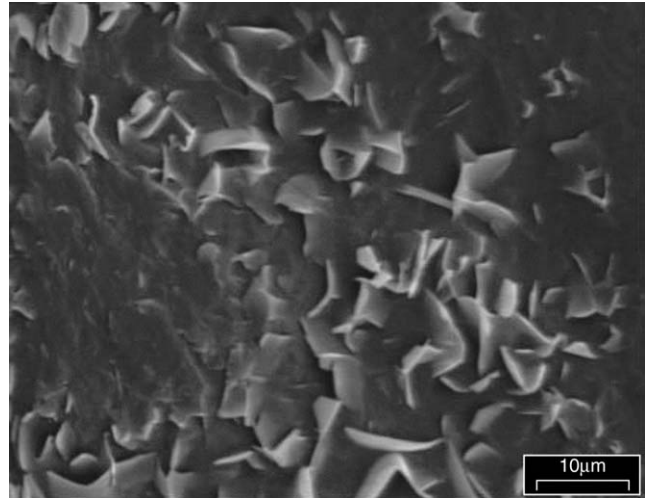


Fig. 7. SEM micrographs of 5%SF-PCL/S surface after 6 months of aging at pH 7.2.

delays the water intake and prevents the swelling of the starch. On the other hand, abiotic aqueous PCL degradation was reported in the literature, but basic pH and high temperature are required [26,27]. In the case of the composites, two factors may be considered: first, the PCL component has the same effect than in the unfilled matrix; second, the present fibre–starch and fibre–fibre interactions prevent the starch chain mobility and the water intake, respectively.

3.4. PCL/S and 15%SF-PCL/S samples in biotic aqueous medium

The effect of the presence of a single bacterial strain on the degradation of PCL/S and 15%SF-PCL/S was evaluated in liquid medium. Fig. 8(a) shows relative changes in composition for PCL/S specimens evaluated from DTG curves obtained after bacterial attack in liquid media. The control composition was invariable with the exposition time but different from the initial one due to the loss of additives, which can easily diffuse into the liquid medium. On inoculated samples, a profuse growth of bacteria was observed during the time of the experiments. Bacteria are thought to be growing on starch, the most readily available component of the blend, although no clear evidence of weight loss was observed in the DTG analysis during at least 2 months. These results indicate that PCL/S is less susceptible to microbial attack in biotic aqueous medium using single bacterial strains than in soil burial, where a mixed population (bacteria and fungi) may act in a synergetic way. This behaviour may be related to the components of the blend. Mater Bi Z is based on PCL and thermoplastic starch [7]. Ishiaku et al. [12] analysed the biodegradation of PCL/sago starch blends in

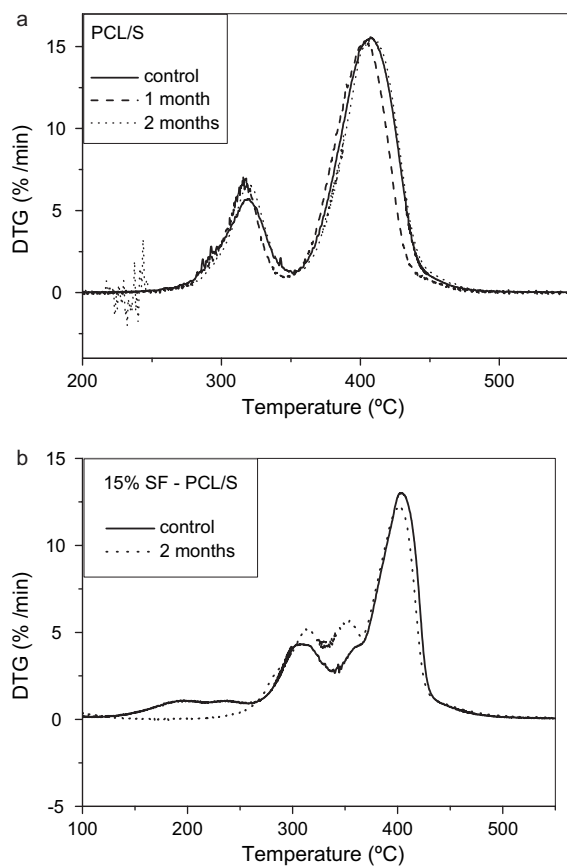


Fig. 8. DTG curves obtained at 10 °C/min under nitrogen atmosphere (a) inoculated PCL/S samples and control (sterile) after 2 months of treatment. (b) Inoculated 15%SF–PCL/S samples and control (sterile) after 2 months of treatment.

aqueous medium and in the presence of the enzyme glucamylase. The authors found that granular sago starch undergoes higher weight loss compared to their thermoplastic counterparts, indicating that deconstructing the starch reduces PCL biodegradability in these conditions [11,12].

Changes in the relative composition corresponding to 15%SF–PCL/S are difficult to evaluate quantitatively, due to the overlapping of the DTG peaks. The results after 2 months of incubation are shown in Fig. 8(b). The main change observed during the 2 months of the experiment was the loss of additives, compared to the sterile control at time zero. However, optical microscopic observations revealed the presence of bacterial biofilms growing on the fibre surface, particularly at locations near the outer edge of the sample where sisal fibres are exposed (Fig. 9). This is most likely associated with the presence of a rougher surface exposed, which favours the microbial attack [28,29]. Degradation starts near the outer edge induced by the presence of the sisal fibres, which promote the water diffusion into the matrix. The same behaviour was also observed during chemical hydrolysis.



Fig. 9. Optical microscopy of 15%SF–PCL/S.

4. Conclusions

The presence of bio-fibres indirectly promotes the degradation of PCL/S in biotic environments. During soil burial, PCL/S showed a sustained weight loss, meanwhile 15%SF–PCL/S presented different stages associated with the formation of fibre–fibre interactions which are responsible for a lag period due to the reduced accessibility to microorganisms. After this period, biodegradation was promoted by the presence of the fibres, which serve as support for the attack of the microorganisms. In addition, channels generated due to the leaching of the low molecular compounds favour the water entrance and the hydrolysis of the starch, the most biosusceptible component. These results allow us to conclude that biodegradation of biocomposites based on PCL/S starts with the consumption of the additives, and low molecular weight products, which result from starch degradation. At later stages of the process, biodegradation of the natural fibres contributes to the increase of the weight loss.

Amilolytic–cellulolytic bacteria selected for the biotic hydrolysis are presumed to be the most efficient scavengers within the soil bacterial population. Nevertheless, the biodegradation rate in liquid media was extremely low as compared to the one observed in soil. The most efficient biodegradation of PCL/S and SF–PCL/S in soil may be attributed to the synergistic action of mixed microbial populations (including bacteria and fungi), present in soil.

PCL/S and sisal fibre composites showed hydrolytic stability in aqueous medium and in the absence of microorganisms, mainly attributed to the hydrophobic character of PCL. The composites showed an unexpected behaviour: composites with low fibre content were less hydrolytically stable than the unfilled matrix,

meanwhile those with higher fibre content showed higher stability. At low fibre content, the fibres are not close enough to produce strong fibre–fibre interactions, but can act as channels to promote water diffusion into the matrix, and as a consequence, the preferential hydrolysis of the starch. At higher fibre content, fibres are able to build up a physical network, which prevents the water intake and enhances the hydrolytic stability of the material.

As shown by the present study, the addition of bio-fibres to PCL/S blends contributes to increasing hydrolytic stability and degradation rate in soil burial.

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