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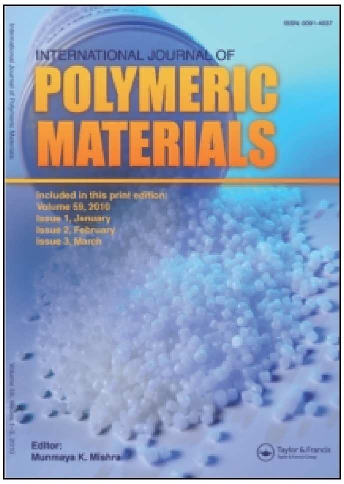

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Bio- and Photo-degradation of Natural Fiber Reinforced Starch-based Biocomposites

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Biocomposites of starch and natural fibers were produced by compression molding. Potato, sweet potato, and corn starch were used as matrices of the biocomposites. Natural fibers including jute, sisal, and cabuya were used as discrete reinforcement. Water, glycerol, glycols, and a chitosan solution were used as plasticizers. Biodegradation was studied using both a compost chamber and a spore solution in an agar-based culture medium. Weight loss was recorded at specific time intervals for the tests of biodegradation in a compost chamber. Microscopical analysis was used to assess biodegradation in agar medium. Photodegradation was studied in a UV degradation chamber. Weight loss was also recorded at specific time intervals. All the biocomposites displayed similar degradation patterns under compost. During the first seven days a marked water absorption tendency was dominant in the weight variation curves. After that period, weight loss became more evident. In the case of UV degradation, a large part of the recorded weight loss was due to a drying effect due to IR radiation and took place mainly during the first seven days. This was taken into account in order to determine the net effect of UV degradation on weight loss.

Keywords: biodegradable polymers, biodegradation in compost and agar medium, optical microscopy, photodegradation

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INTRODUCTION

The three main reasons for the development of biocomposites are: (i) they can be produced from renewable resources, (ii) they are biodegradable, and (iii) they “might” be cheap. In previous articles the authors have reported the mechanical, thermal, and structural properties of this type of composite material [1]. In this third part of a series, the bio- and photo-degradation characteristics of natural fiber reinforced starch based biocomposites are studied.

BIODEGRADATION AND PHOTODEGRADATION

Biodegradation

Natural macromolecules (e.g., protein, cellulose, and starch) are generally degraded in biological systems by hydrolysis followed by oxidation. The biological environment, that is, the biological surroundings in which polymers are present, includes the biological agents responsible for the deterioration of polymeric substances. Biological agents such as bacteria, fungi, and their enzymes consume a substance as a food source so that its original form disappears. Under appropriate conditions of moisture, temperature, and oxygen availability, biodegradation is a relatively rapid process [2].

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Photodegradation

Photodegradation is promoted by irradiation (e.g., sunlight), and it rarely leads to complete removal. Most plastics tend to absorb high-energy radiation in the ultraviolet portion of the spectrum, which results in the formation of free radicals and causes oxidation, extraction, and other degradative reactions [3–5].

EXPERIMENTAL

Materials

The composites were made out of native starch, plasticizers, and natural fibers. Potato, sweet potato, and corn starch were used. Starch granules were observed under polarized light and particle shape and dimensions were recorded. Water, glycerol, ethylene glycol, propylene glycol, and a chitosan solution were used as plasticizers in concentrations up to 10% by weight. Sisal, Jute, and Cabuya were used as reinforcing fibers in lengths in the range 4–6 mm. Before processing, all fibers were washed with 3% non-ionic detergent at 70°C during 1 h, then washed with distilled water and dried in an oven at 65°C for 24 h. Fiber contents in the range 0–15% w/w were used in the composites.

Sample Preparation

Starch blends were prepared by mixing native starch with the plasticizing agent. Fibers were added to the mixture and mixing continued until no major clumps could be observed. A thermoregulated compression molding press was used to prepare the specimens. A simple male–female mold with dimensions 110 mm × 19 mm × 6 mm was used to prepare the specimens for mechanical characterization. The following processing temperatures were used: 130, 150, and 175°C. Processing times varied between 25 and 45 min.

Experimental Methods

Biodegradation Tests in Compost

Biodegradability tests were undertaken using ASTM standards D5338 [6] and D5509 [7] as a guideline. Most standard test methods for the study of biodegradation under controlled composting conditions call for mature compost as an inoculum in order to obtain significant results [2]. The environmental conditions for the different tests were: $20 \pm 2°C$ and $80 \pm 5\%$ relative humidity (HR). The specimen dimensions were chosen in order to obtain enough mass to produce carbon dioxide (CO_2) to react with compost organisms. Laminar specimens with a surface of 1.0 cm^2 were found to be adequate for testing purposes.

The compost chamber was filled with 600 g of compost. Before the specimens were buried in compost, their initial weight was recorded. While the tests were running, air at a relative humidity of 80% HR was injected into the compost chamber in order to maintain a specific humidity that allows the micro-organisms in the compost to progress adequately and to prevent the compost from decomposing. The specimens were withdrawn at specific periods of time, washed for 5 minutes in 100 ml of $HgCl_2$ 1 ppm, rinsed in ethanol for 2 min and air dried for 12 h.

In order to isolate the effects of moisture absorption during the test and the actual weight loss due to biodegradation, a calibration baseline had to be made for each type of specimen. Water absorption tests were carried out to that end using the same specimens as in the compost biodegradation tests. Three repeats were used for each condition.

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Biodegradation Tests in Agar Medium

Samples of starch-glycerine reinforced with sisal fibers processed at 175°C during 30 min and pellicles of starch plasticized with chitosan were used in this type of experiments.

In order to prepare a spore solution, 50 g of farm land and 150 ml of milliQ water were mixed. The solution was filtered and precipitated for 30 min. For inoculating, 1 ml of this solution was added to each Petri dish containing the samples and pellicles. In addition, two types of culture media were prepared. The reference agar medium comprised the following: 0.7 g/l KH_2PO_4, 0.7 g/l $MgSO_4 \cdot H_2O$, 1.0 g/l NH_4NO_3, 0.005 g/l NaCl, 0.002 g/l $FeSO_4 \cdot H_2O$, 0.002 g/l $ZnSO_4 \cdot H_2O$, O, 0.001 g/l $MnSO_4 \cdot H_2O$ and 15.0 g/l agar. The nutrient agar medium was prepared by adding 10 ml of B5 vitamin to the reference agar medium. Thus 0.1 g myo-inositol, 0.001 mg pyridoxine-HCl, 0.01 g thiamine-HCl, and 0.001 g nicotinic acid were added. The reference agar medium was used for the chitosan-starch specimens because these contained high values of nitrogen and carbon, whereas the nutrient agar medium was used for the natural fiber reinforced starch specimens. All media were autoclaved for 35 min and 15 min at 120°C. Incubation was realized at 30°C with pH 4.2 because the growth of fungi and bacteria is improved in acid media.

Microscopical analysis was used in order to assess the quantities of colonies that the samples displayed after 2, 5, 7, and 9 days of exposition in the media. For eliminating the colonies, the samples of starch reinforced with sisal fibers were washed in an $HgCl_2$ $(1 + 1000)$ solution for 5 min, rinsed in alcohol and dried at 20°C. The pellicles were washed by dispersing the solution onto the surface. Then, they were rinsed in an alcohol–water solution and placed on glass for drying.

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Photodegradation

Photodegradation tests were carried out using accelerated exposure under UV radiation, according to ASTM D4329 [8]. After specimens were exposed, weight loss and changes in structure and morphology were recorded.

For photodegradation tests, an environmental chamber (0.30 m × 0.50 m × 0.30 m) fitted with a Phillips fluorescent UV (100 W) lamp was used. The temperature during the entire test was in the range 18–27°C, and the specimens remained at a constant distance of 0.30 m from the lamp. Four specimens from every mixture type were studied for replication purposes.

Specimens with dimensions 110.0 mm × 19.0 mm × 6.0 mm were chosen in order to obtain an adequate test area.

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Exposure periods of 24 h a day for 4 weeks (28 days) were chosen in order to observe the effects of degradation. For specimens, the initial weights were recorded and withdrawn after finishing the exposure cycle to observe the weight loss and changes in structure.

It was due to the infrared radiation involved in the exposure that specimens showed high dryness levels. This weight loss due to infrared exposure was calculated measuring the humidity loss for the period of exposure mentioned. A vacuum oven, with silica gel as dessicator, at 20°C was used in order to measure humidity loss. The specimens remained in the oven for 7 days, but after the third day, humidity loss reached a plateau.

Both effects, UV radiation and humidity loss due to infrared radiation, were taken into account to study the effect of photo degradation.

A trinocular Brunel Stereomicroscope model BMZ was used to assess bio- and photodegradation. A stain solution for observing the pellicles in the microscope was prepared as follows: 6 g KI and 2 g I_2 were mixed in 100 ml of water. Then, 1 ml of this solution was dissolved in 10 ml of water. Two drops of the stain solution were added onto the surface of a 10 mm × 10 mm piece of the pellicle. It was dried and observed in an optical microscope. Samples of starch reinforced with sisal fibers were observed directly. Moreover, a high vacuum Phillips scanning electron microscope (SEM) was used to characterize biodegraded surfaces in the specimens. The procedure used for sample preparation was described by Torres and Diaz [9]. Briefly, the samples were cut from the biodegraded specimens and then gold coated. Beam voltages between 5 and 15 kV were used.

RESULTS AND DISCUSSION

Biodegradation in Compost

The weight loss curves from compost biodegradation tests of starch biocomposites produced with different types of starch can be observed in Figure 1. In this case, mixtures with 5% of sisal fibers used as reinforcement were tested. Results showed that corn starch specimens present higher degradation rates than the other starch based biocomposites.

Figure 2 shows the weight increase during the first week followed by a progressive weight loss for starch biocomposites with varying fiber concentrations. After 40 days, the average weight loss was 14.3%. It is shown that at increasing fiber content, biodegradation rates tend to increase. This might due to the fact that composites containing higher fiber contents tend to form several voids, hence

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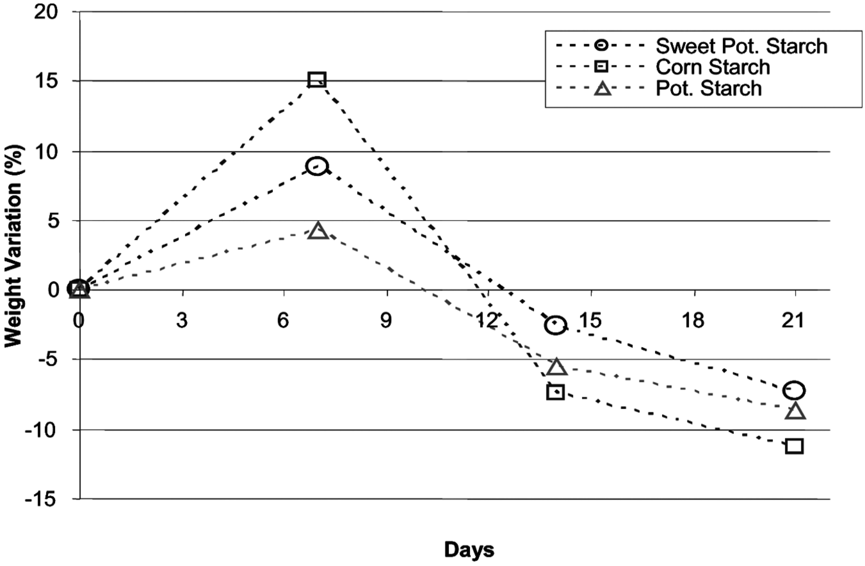

FIGURE 1 Compost biodegradation curves for starch biocomposites (90% starch, 5% sisal, and 5% glycerine) with different types of starch. Processing temperature: 175°C and processing time: 35 min.

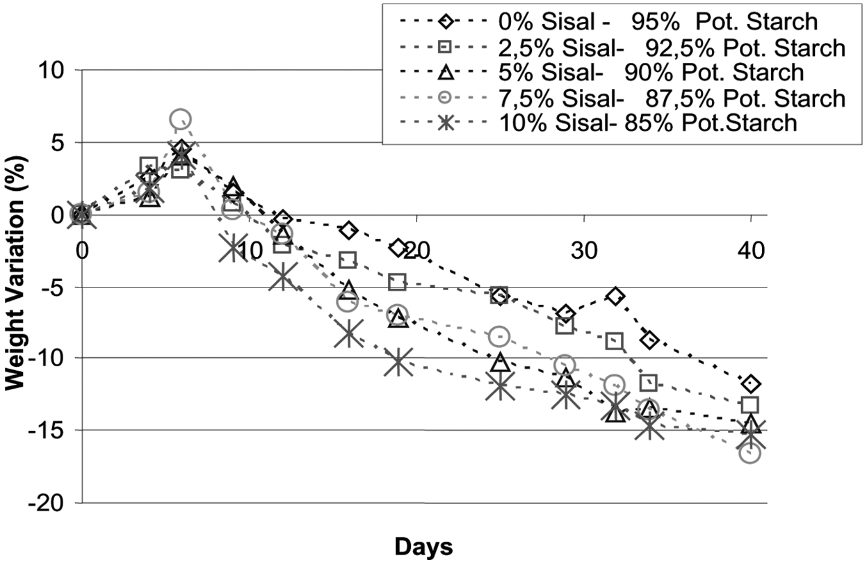

FIGURE 2 Compost biodegradation curves for starch biocomposites (5% glycerine) with varying sisal fiber content. Processing temperature: 175°C and processing time: 35 min.

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increasing the effective area in which biodegradation takes place. Also, in Figure 2, reinforcing fibers showed no significant effect on moisture absorption during the first week. Results showed that at varying potato starch percentages, the biodegradation behavior of the different composites remained almost similar.

In Figure 3 it can be observed that at increasing fiber contents, moisture absorption does not vary considerably. For the different composites, the moisture absorption was not markedly different from one another. After 35 days, the weight gain percentage of the composites, due to humidity absorption, was 22.5% on average. Such high moisture absorption levels may be associated with the combined hydrophilic characteristics of both fibers and matrix.

Figure 4 shows the weight loss for potato starch biocomposites (10% w/w fiber content) with different types of reinforcing fibers. Jute and Cabuya reinforced composites showed the highest weight loss after 21 days (13–15%) compared to sisal reinforced composites (5%).

In Figure 5 it is shown that from day 1 to 7, all specimens gained weight due to moisture absorption from the environment. After 7 days, weight loss due to biodegradation tends to increase. A similar tendency can be observed for all types of biocomposites. After 7 days, all specimens presented almost the same weight increment (5%) whereas

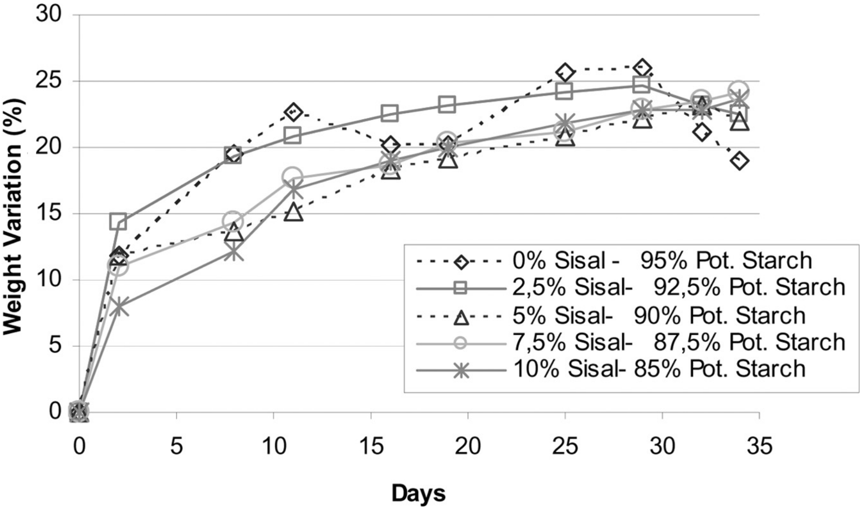

FIGURE 3 Moisture absorption curves for starch biocomposites (5% glycerine) with varying sisal fiber content. Processing temperature: 175°C and processing time: 35 min.

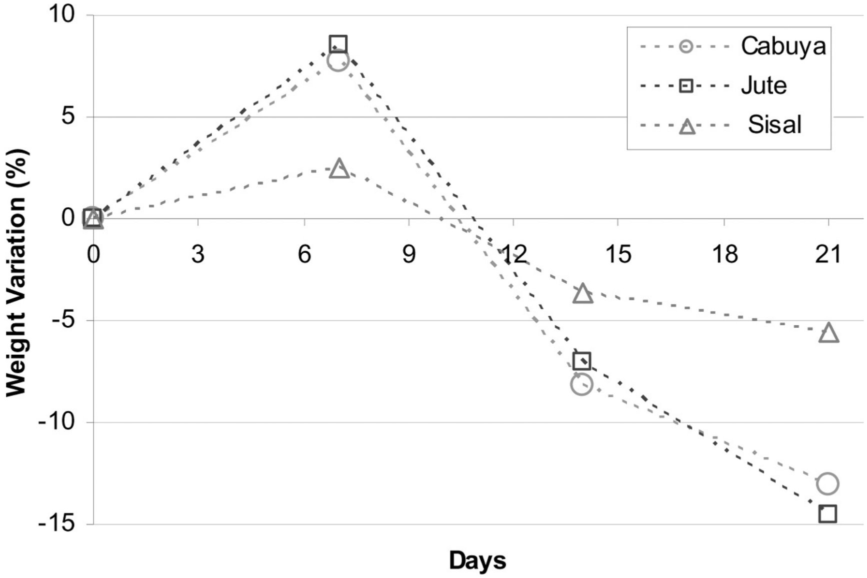

FIGURE 4 Compost biodegradation curves for starch biocomposites (85% potato starch, 5% glycerine) with different types of reinforcing fibers (10%). Processing temperature: 175°C and processing time: 35 min.

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after 30 days the average weight loss was around 16%. The effect of plasticizer content on the weight loss due to biodegradation was not significant. This is confirmed by the closely packed weight loss curves (Figure 5) obtained for all specimens.

Moisture absorption does not vary considerably with glycerine content as can be observed in Figure 6. A similar degradation pattern can be observed for all specimens. It can be observed that the highest moisture absorption rates occur for reinforced composites containing 5% of glycerine. It might actually be that the higher starch content in those composites is what produces high moisture absorption.

The effect of using different plasticizers on the weight loss behavior due to biodegradation is shown in Figure 7. It is observed that the biocomposites with propylene glycol and ethylene glycol displayed the highest weight increments for the first week, whereas water-based biocomposites showed the lowest weight increments. On the other hand, the specimens plasticized with ethylene glycol presented the highest weight loss (17%).

Figure 8 shows that with increasing processing temperatures, the final weight loss of potato starch–sisal biocomposites decreased.

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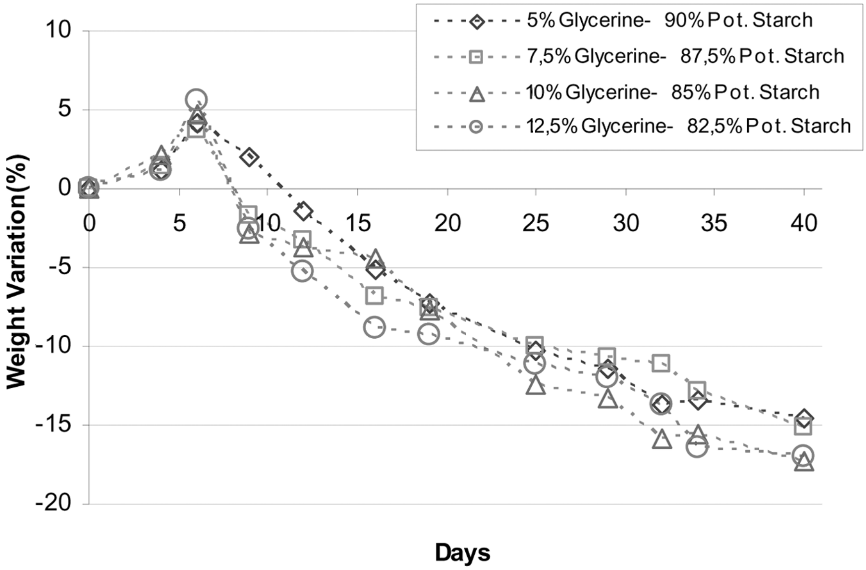

FIGURE 5 Compost biodegradation curves for starch biocomposites (5% sisal fibers) with varying contents of glycerine. Processing temperature: 175°C and processing time: 35 min.

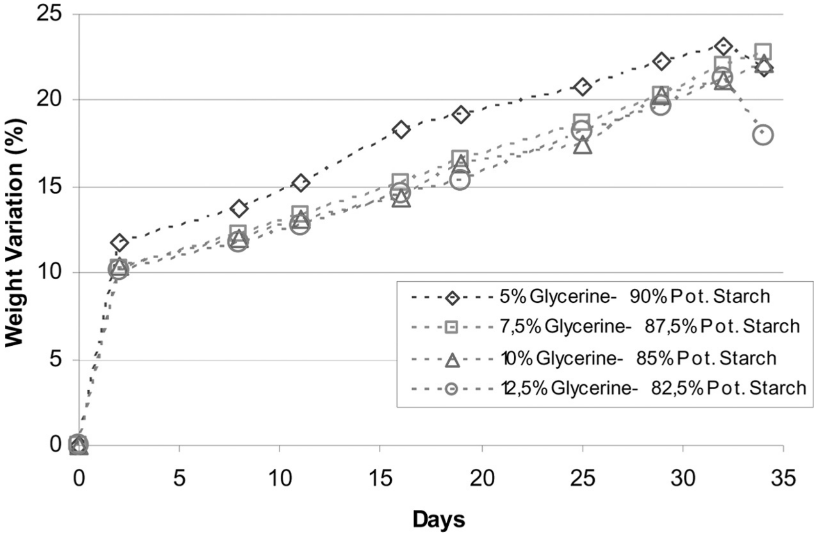

FIGURE 6 Moisture absorption curves for starch biocomposites (5% sisal fibers) with varying contents of glycerine. Processing temperature: 175°C and processing time: 35 min.

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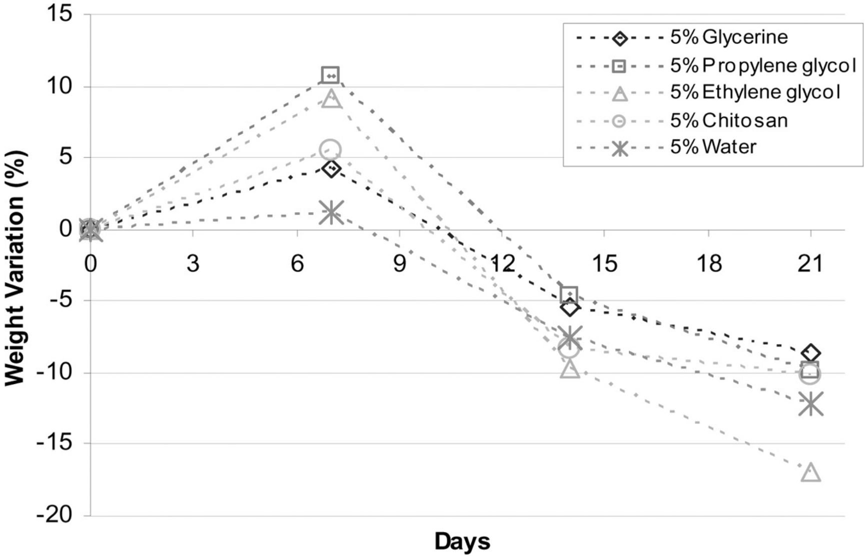

FIGURE 7 Compost biodegradation curves for starch biocomposites (90% potato starch and 5% sisal fibers) with different types of plasticizer. Processing temperature: 175°C and processing time: 35 min.

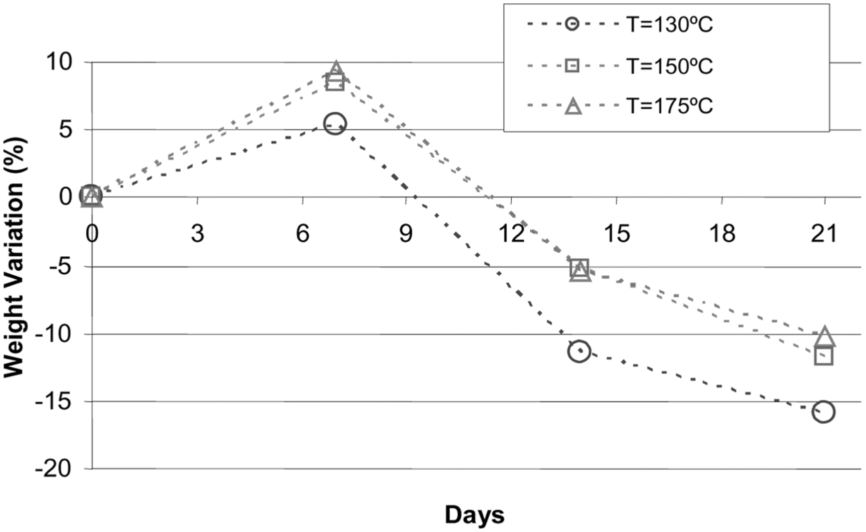

FIGURE 8 Compost biodegradation curves for starch biocomposites (90% potato starch and 5% sisal fibers, 5% glycerine) with varying processing temperatures. Processing time: 35 min.

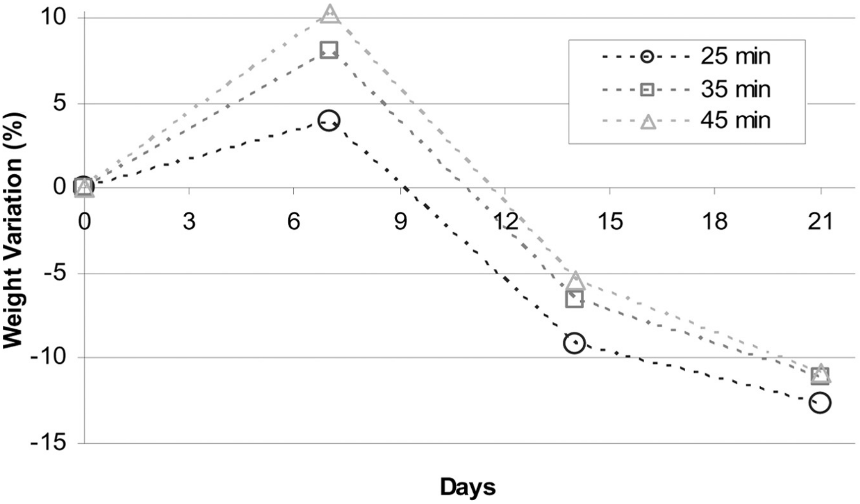

FIGURE 9 Compost biodegradation curves for starch biocomposites (90% potato starch and 5% sisal fibers, 5% glycerine) with varying processing times. Processing temperature: 175°C.

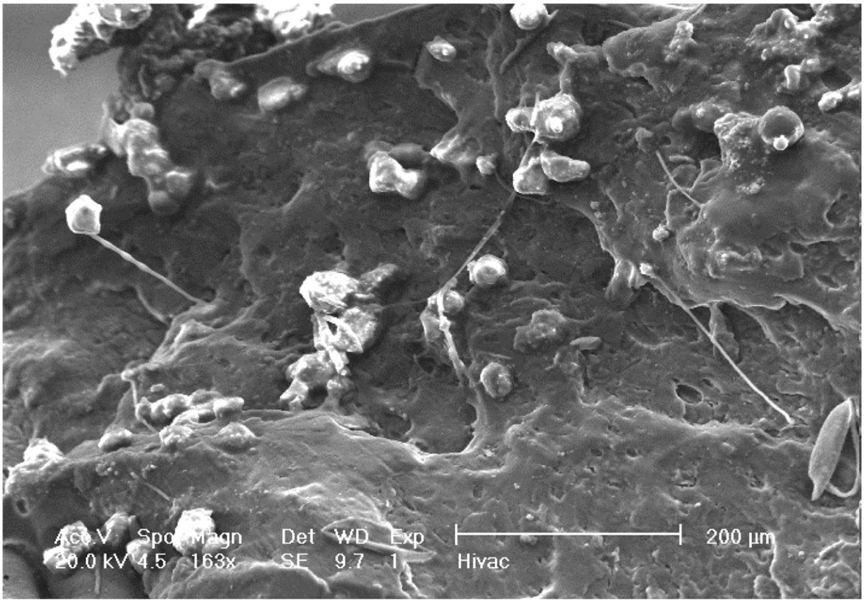

FIGURE 10 SEM picture of a biodegraded unreinforced potato starch specimen (95% potato starch, 5% water).

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However, moisture absorption between days 1 to 7 was higher for the specimens prepared at higher processing temperatures.

From Figure 9 it can be observed that higher processing times correspond to higher weight gains due to moisture absorption. Final weight loss for all specimens decreased with increasing processing times, although there was no significant difference among the final weight losses for the different specimens.

Figure 10 shows an SEM picture of a biodegraded sisal reinforced potato starch specimen. Micro-organisms found in compost can be observed on the surface of the specimen.

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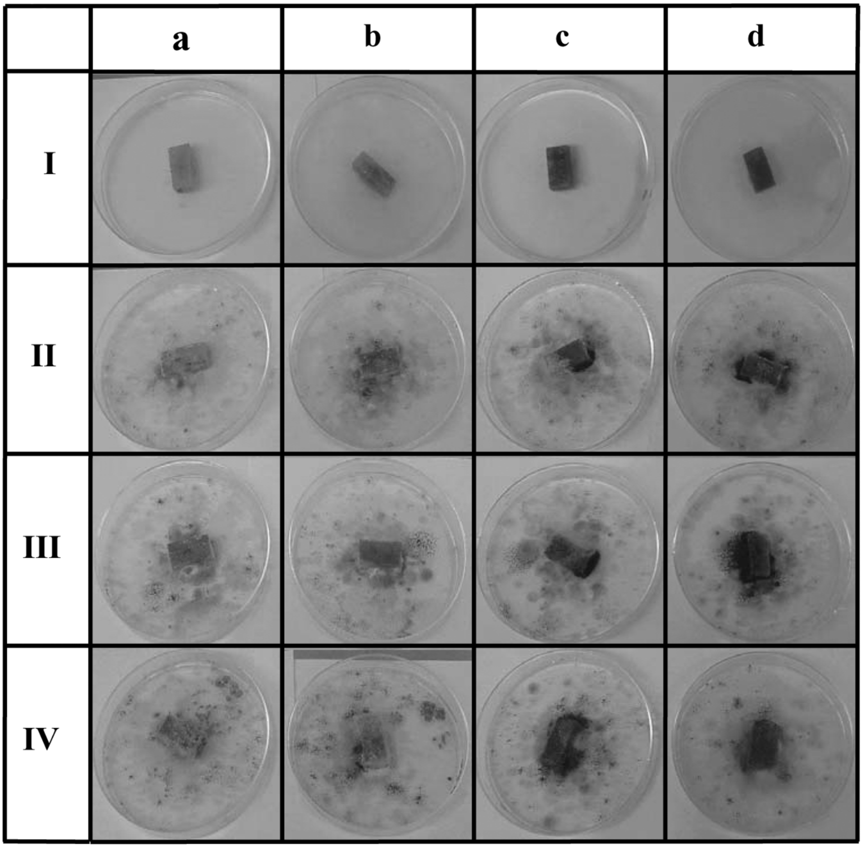

FIGURE 11 Samples of sisal starch composites at fiber contents of (a) 0, (b) 2.5, (c) 5.0, and (d) 7.5% w/w with 5% glycerine at (I) 2, (II) 5, (III) 7, and (IV) 9 days of exposition in agar medium.

Biodegradation in Agar Medium

From Figure 11, it can be observed that there is a tendency in the formation of colonies in starch fibers composites: the higher the fiber content, the higher the number of colonies. This can be attributed to void formation, a process that takes place at higher fiber contents. In this case, micro-organisms have more effective area for biodegradation to occur. In addition, higher contents of glycerine promote the formation of colonies in the composites as can be observed in Figure 12.

From Figure 13, it can be observed that for short periods of time exposure in agar medium of the sisal reinforced composites, matrices

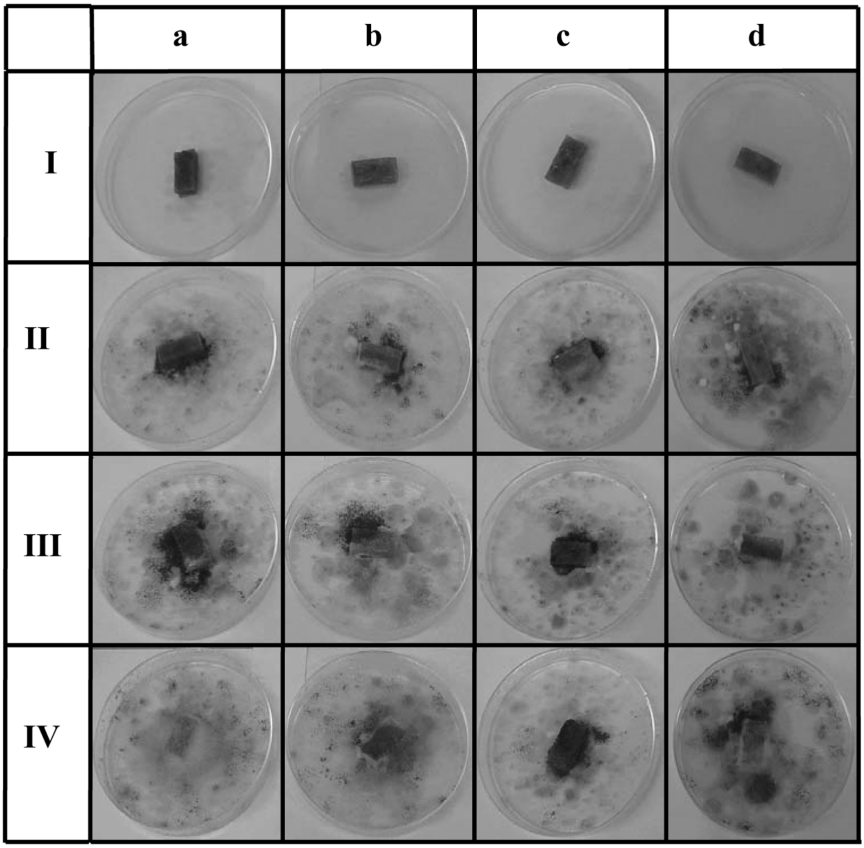

FIGURE 12 Samples of sisal starch composites at fiber content of 5% w/w and at glycerine contents of (a) 5, (b) 7.5, (c) 10 y, (d) 12.5% w/w at (I) 2, (II) 5, (III) 7 and (IV) 9 days of exposition in agar medium.

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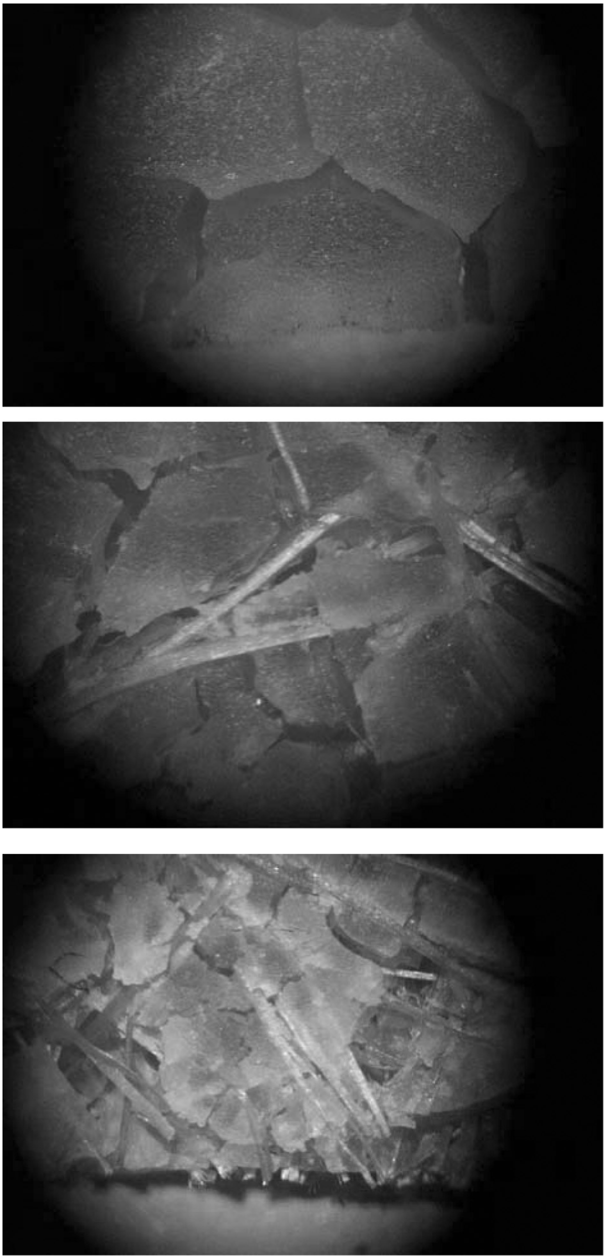

FIGURE 13 Samples of sisal reinforced composites showing deterioration of the matrix and fibers out of the surface. Time of exposure in agar medium: 10 days.

show deterioration and fibers can be observed out of the surface of the composites. Moreover, sisal fibers apparently show no deterioration.

Photodegradation

Figure 14 shows that at increasing fiber content, the weight loss rates were similar for all reinforced composites. Hence, there is no significant interdependence between fiber content and photodegradation. After 7 days, the weight loss was 14.5% in average, whereas, the final loss after 28 days was 15.6% approximately.

As may be observed from Figure 15, the weight loss rate is highest during the first 7 days (15% in average). After day 7, weight is lost at a much slower rate, almost reaching a plateau. The final weight loss after 28 days was 16% in average. Figure 15 also shows that with higher glycerine contents, higher weight losses were observed.

Figure 16 shows the net effect of the UV radiation. Data obtained from the drying curves were subtracted from the data measured at the UV tests. Results showed that the net UV effect after 7 days was weight loss of 6.2% on average, and 7.2% on average at the end

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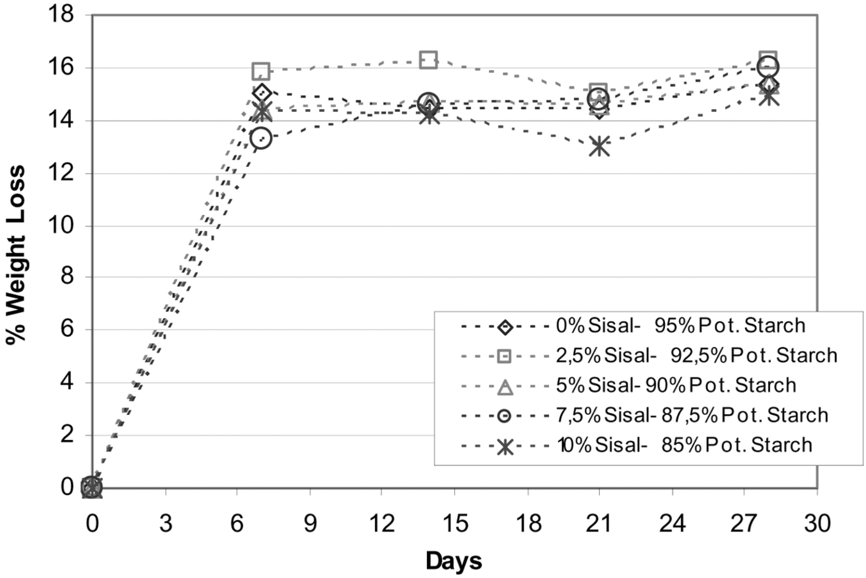

FIGURE 14 UV degradation weight loss curves for different starch biocomposites (5% glycerine) with varying sisal fiber contents. Processing temperature: 175°C and processing time: 35 min.

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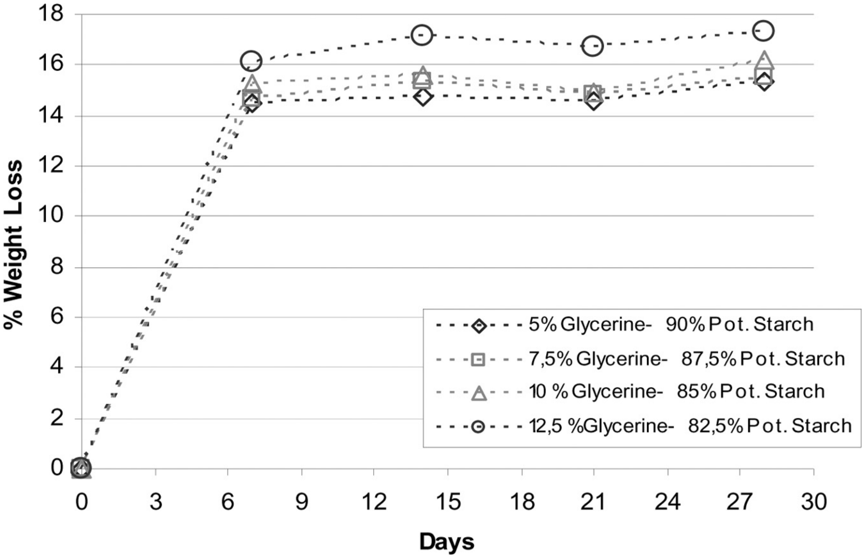

FIGURE 15 UV degradation weight loss curves for different starch biocomposites (5% sisal) with varying glycerine content. Processing temperature: 175°C and processing time: 35 min.

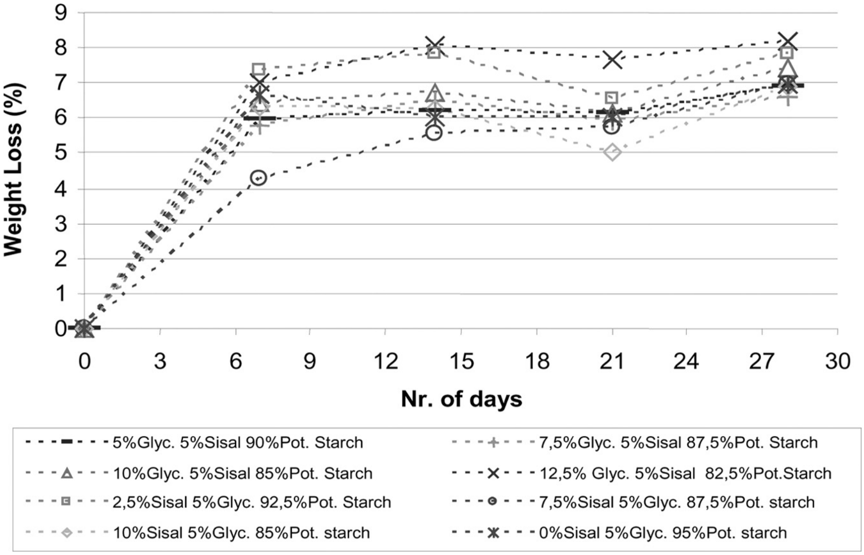

FIGURE 16 Net effect of UV radiation of weight loss for different starch biocomposites.

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of the test (day 28). This shows that a large part of the net weight loss occurs during the first week.

It was also found that, in average, the effect of UV degradation on the weight loss of the specimens was in the order of 43%, whereas the remaining weight loss (53%) was due to drying of the specimens due to IR radiation.

CONCLUSIONS

Biodegradation studies in agar and compost media and photodegradation studies in a UV environmental chamber were carried out on different types of natural fiber reinforced starch-based biocomposites.

Weight loss curves indicated that all the biocomposites displayed similar biodegradation patterns under compost. During the first 7 days, a marked water absorption tendency was dominant in the weight variation curves. After that period, weight loss became more evident and could be attributed mainly to biodegradation. It seems that biodegradation of the biocomposites was determined mainly by the starch phase of the material. This is based on the fact that fiber or plasticizer content did not affect the shape of the weight loss curves of the biocomposites, which were rather similar to those of the unreinforced starch samples. In addition, from the microscopical analysis of the fiber starch composites, it can be observed that at high contents of fibers and glycerine, the number of colonies is increased. In the case of UV degradation, a large part of the recorded weight loss was due to a desiccating effect due to IR radiation and took place mainly during the first 7 days. This was taken into account in order to determine the net effect of UV degradation on weight loss. Weight loss due to UV degradation was estimated as 43% of the total weight loss.

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