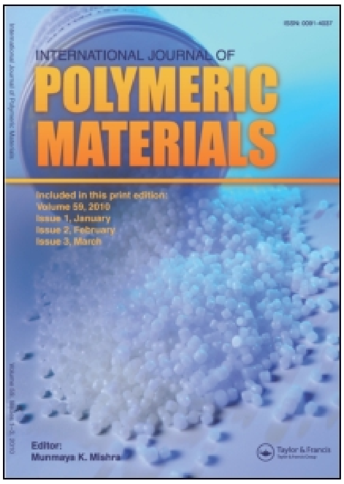

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Thermal and Structural Analysis of Natural Fiber Reinforced Starch-Based Biocomposites

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This is the second part of a series of articles dealing with characterization of starch based biodegradable composites. Potato, sweet potato, and corn starch varieties were used as matrices of the biocomposites. Natural fibers including jute, sisal, and cabuya were used as discrete reinforcement. Water and glycols were used as plasticizers. Compression molded specimens were prepared and characterized by a variety of techniques. Differential Scanning Calorimetry (DSC) and Thermogravimetry (TGA) were used to characterize the thermal behavior of these composites. Processed specimens did not show the typical endothermic peak observed in DSC scans for native starch powder. No significant difference was observed for weight loss and decomposition due to fiber or plasticizer content among the different specimens. Attenuated Total Reflectance–Infrared Spectroscopy (ATR-IR) was used to characterize the starch compounds and the effect of plasticizers and reinforcing fibers. The spectra found for most specimens were consistent with those of pure starch. Scanning electron microscopy (SEM) pictures showed the morphology of the specimens for different types of starch matrices and different fiber contents.

Keywords: compression molding, natural fiber composites, starch polymers, structural analysis, thermal analysis

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INTRODUCTION

The search for biodegradable compostable composite materials is one of the most relevant issues in modern polymer technology, due to a continuously increasing environmental pressure. These materials should be produced from natural and renewable resources instead of oil and hydrocarbon derivatives. They should be compostable and not contribute to the increasing amount of nonbiodegradable plastic that pollutes the environment. Starch-based composites have proved to offer a possible solution to this problem [1–5]. Most of the available research has been performed on corn starch [1–3].

Previous articles from this laboratory have reported the mechanical and degradation properties of starch-based composites from a variety of native starch sources and natural fibers [6–7]. This article is the second of a series dealing with the characterization of starch-based biocomposites. In the present article, some thermal properties of starch-based biocomposites have been studied using differential scanning calorimetry (DSC) and thermogravimetry (TGA). Attenuated Total Reflectance—Infrared spectroscopy (ATR-IR) was used to characterize the starch compounds and the effect of plasticizers and reinforcing fibers. The morphology of the composites was observed with SEM.

THERMAL PROPERTIES OF STARCH COMPOUNDS AND COMPOSITES

The thermal properties of starch have been studied by several authors [8–10]. The thermal properties of starch-based composites reinforced with wood flour were investigated by Curvelo et al. using DSC and TGA to characterise transition temperatures and thermal degradation, respectively [11–12]. Averous and Boquillon have studied different natural fiber reinforced starch composites using dynamic mechanical thermal analysis (DMTA) as well as TGA for characterizing the thermomechanical properties and thermal degradation, respectively [13].

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 (Figure 1). Water, glycerol, ethylene glycol, propylene glycol, and chitosan in solution were used as plasticizers in

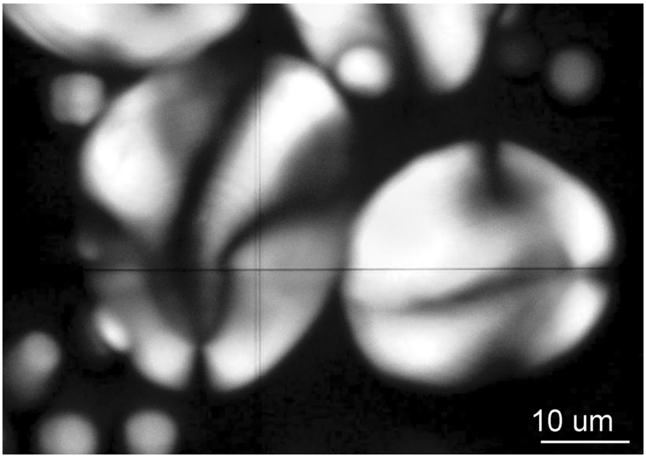

FIGURE 1 Potato starch granules showing the common Maltese cross structure under polarized light.

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.

Preparation of the Specimens

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.

Table 1 shows the different compositions used in the experiments.

Attenuated Total Reflectance—Infrared Spectroscopy (ATR-IR)

A Thermoelectron Corporation spectrophotometer was used in the experiments. The number of scans was 80 and the resolution was 8. The software used was Omnic, including a correction for H_2O and CO_2.

TABLE 1 Compositions (Mixtures) of the Starch Based Biocomposites Used in the Experiments

Mixture Nr	Type and content of starch (%)	Type and content of plasticizer content (%)	Type and content of fibers (%)
1	90% Potato starch	5% Glycerine	5% Cabuya
2	90% Potato starch	5% Glycerine	5% Sisal
3	90% Potato starch	5% Glycerine	5% Jute
4	90% Potato starch	5% Water	5% Sisal
5	95% Potato starch	5% Water	0%
6	90% Potato starch	5% Chitosan	5% Sisal
7	95% Potato starch	5% Chitosan	0%
8	90% Potato starch	5% Propylene glycol	5% Sisal
9	95% Potato starch	5% Propylene glycol	0%
10	90% Potato starch	5% Ethylene glycol	5% Sisal
11	95% Potato starch	5% Ethylene glycol	0%
12	90% Corn starch	5% Glycerine	5% Sisal
13	90% Sweet potato starch	5% Glycerine	5% Sisal
14	100% unprocessed sweet potato starch	—	—
15	100% unprocessed corn starch	—	—
16	100% unprocessed potato starch	—	—

Differential Scanning Calorimetry (DSC)

A Metler Toledo Star DSC was used for the experiments. An N_2 atmosphere was used in all cases. Two temperature scans were carried out with the specimens; the first scan was performed in the range 30°C to 190°C and the second one in the range -100°C to 250°C. The scanning rate was 10°C/min in both cases. The analysis was performed on the first scan because the second scan showed signs of partially degraded samples. This was confirmed by TGA data.

Thermogravimetry (TGA)

A Perkin Elmer TGA analyzer with Pyris 3.8 software was used. Tests were carried out using both O_2 and Ar atmospheres. Temperature ranges were 25°C–600°C, with a temperature increment 10°C/min in both cases.

Microscopical Characterization

A high vacuum Phillips scanning electron microscope (SEM) was used to characterize the structure of the biocomposites. The specimens were frozen in liquid nitrogen and then broken. Fracture surfaces were examined as described by Torres et al. [14–15]. Starch granules were observed by polarized light optical microscopy.

RESULTS AND DISCUSSION

Attenuated Total Reflectance–Infrared Spectroscopy (ATR–IR)

ATR-IR spectra of most of the biocomposites are very similar, as may be observed from comparing the spectra for mixtures 4 in Figure 2, and those for mixtures 4 and 5 in Figure 3. The presence of fibers might be hidden by that of starch or it is not detected during the test because ATR-IR scans only the surface of the specimens. It is possible that the fibers are in the interior of the specimens, or if they are on the surface, they might be covered with starch. IR spectrum for unprocessed starch (16 in Figure 2) is the one that differs the most from the processed biocomposites; however, the basic structural peaks can be observed in all cases. Processing conditions of the samples may be responsible for this difference, as it is known that thermal changes occur in starch (dehydration, gelatinization, etc.) [16]. This difference was also evidenced in TGA measurements.

Mixture 7 (Figures 4 and 5), containing 5% chitosan, shows a similar spectrum to that of pure starch (mixture 5 in Figure 3, and mixture

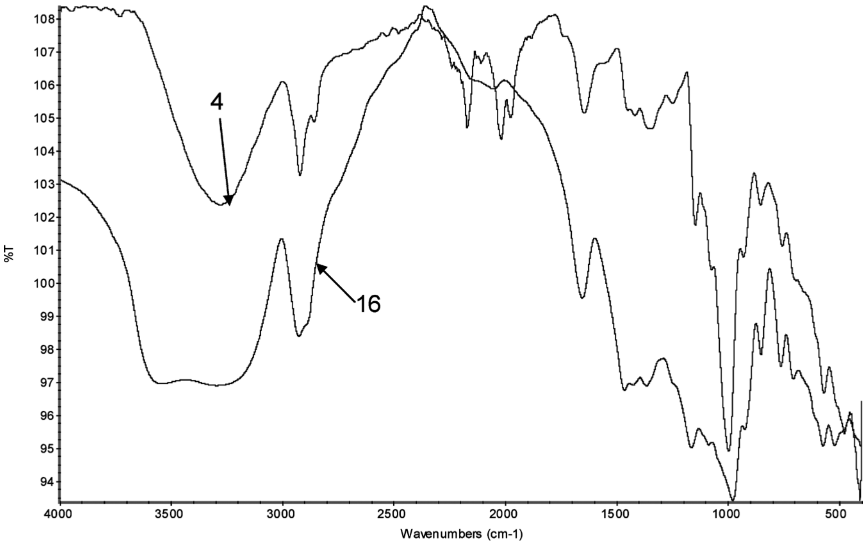

FIGURE 2 ATR-IR spectra of mixture 4 (90% potato starch, 5% sisal, 5% water) compared to unprocessed pure potato starch (mixture 16).

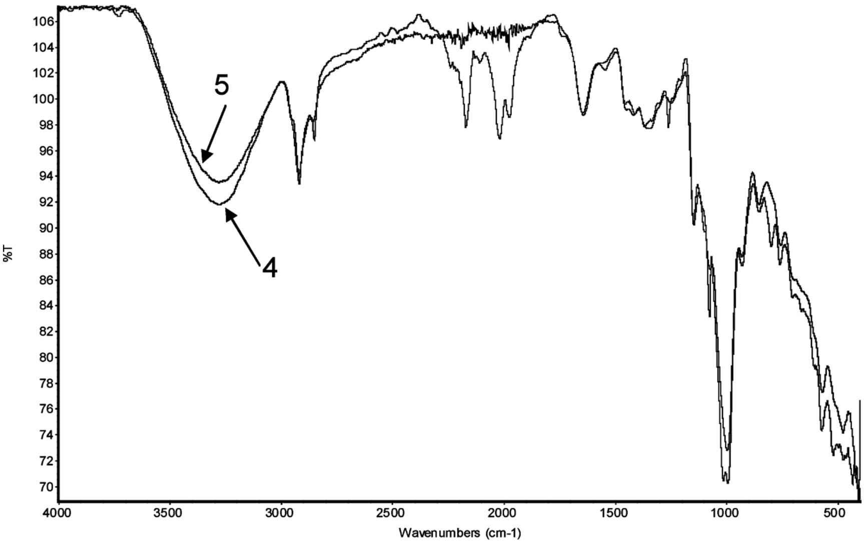

FIGURE 3 ATR-IR spectra of mixture 4 (90% potato starch, 5% sisal, 5% water) compared to mixture 5 (95% potato starch, 5% water).

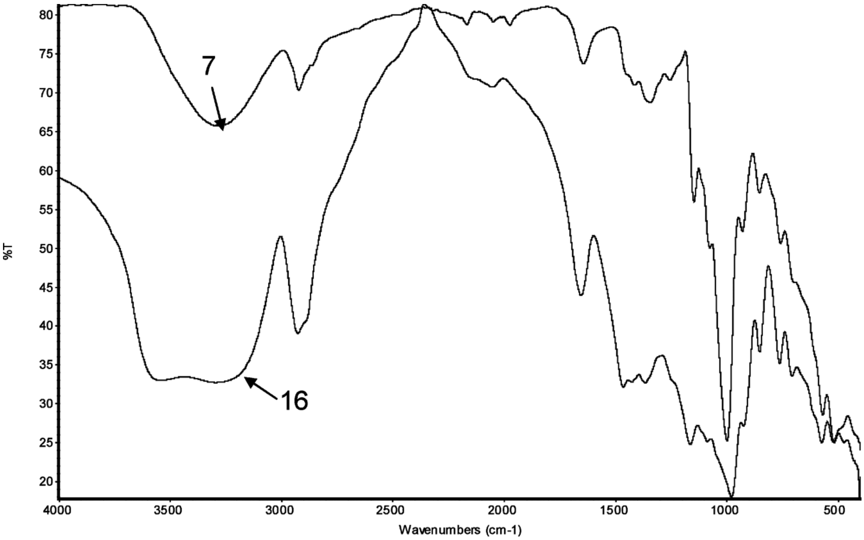

FIGURE 4 ATR-IR spectra of mixture 7 (95% potato starch, 5% chitosan) compared to unprocessed pure potato starch (16).

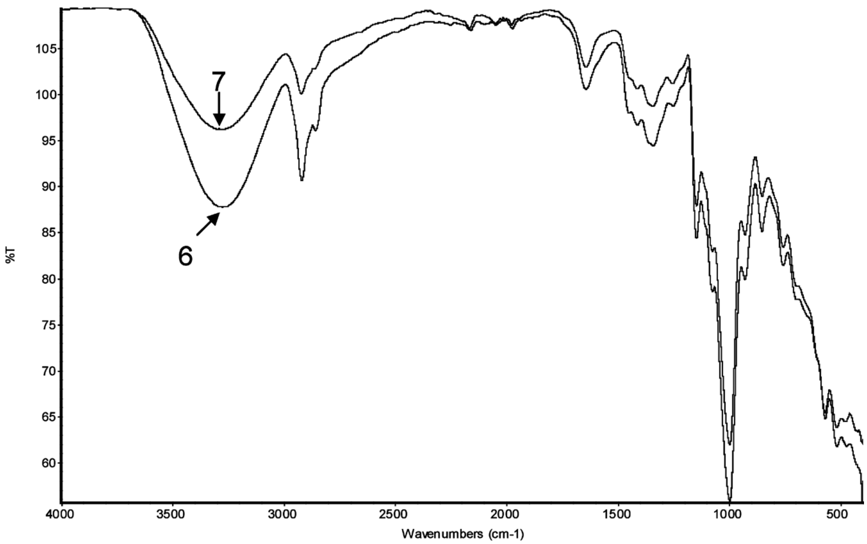

FIGURE 5 ATR-IR spectra of mixtures 6 (90% potato starch, 5% sisal, 5% chitosan) and 7 (95% potato starch, 5% chitosan).

16 in Figure 4). Absorption bands corresponding to chitosan hydroxyl groups could be hidden by those of starch; however, the absorption due to carbonyl groups in chitosan would be expected to be apparent around 1500 and 1700 cm^{-1} [17]. Therefore, it seems that chitosan is not near the surface of the sample. Something similar occurs when glycerol was part of the composition.

It is clear that processed corn and potato starch have similar functional groups because their IR spectra are practically the same. These spectra are similar to the ones obtained from corn starch samples prepared in KBr pellets reported by Mano et al. [18].

Differential Scanning Calorimetry (DSC)

Figure 6 shows a DSC graph displaying results for unprocessed potato starch (mixture 16 from Table 1). From left to right in the graph, the following temperature scans can be observed: heating from 25 to 200°C, cooling from 200 to 20°C, and a second heating scan from 20 to 270°C. From the first heating scan, part of a broad endothermic peak can be observed in the range 30–190°C. This type of peak is similar to those reported in the literature for different types of starch, including potato starch [8–10]. Figures 7 and 8 show DSC scans

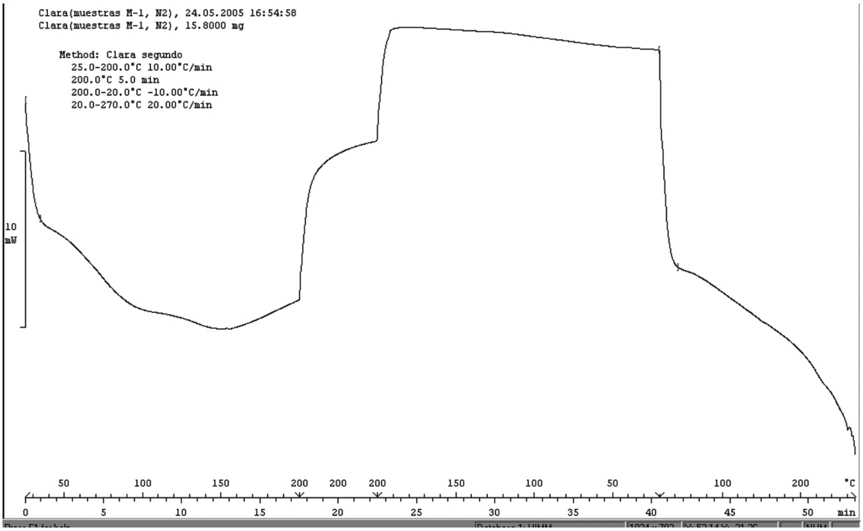

FIGURE 6 DSC scans (first heating ramp, cooling, second heating ramp) obtained for unprocessed native potato starch.

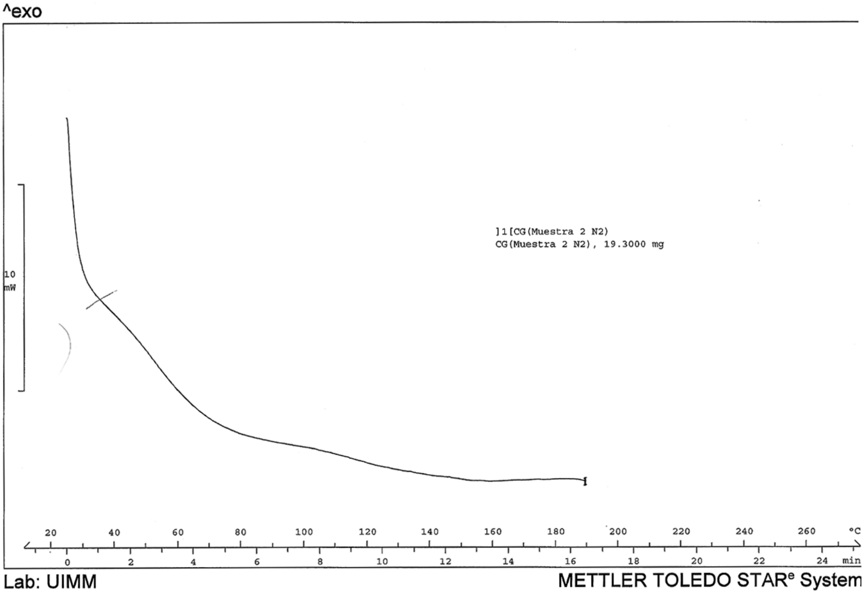

FIGURE 7 DSC scan obtained for mixture 2 (90% potato starch, 5% glycerol, 5% sisal).

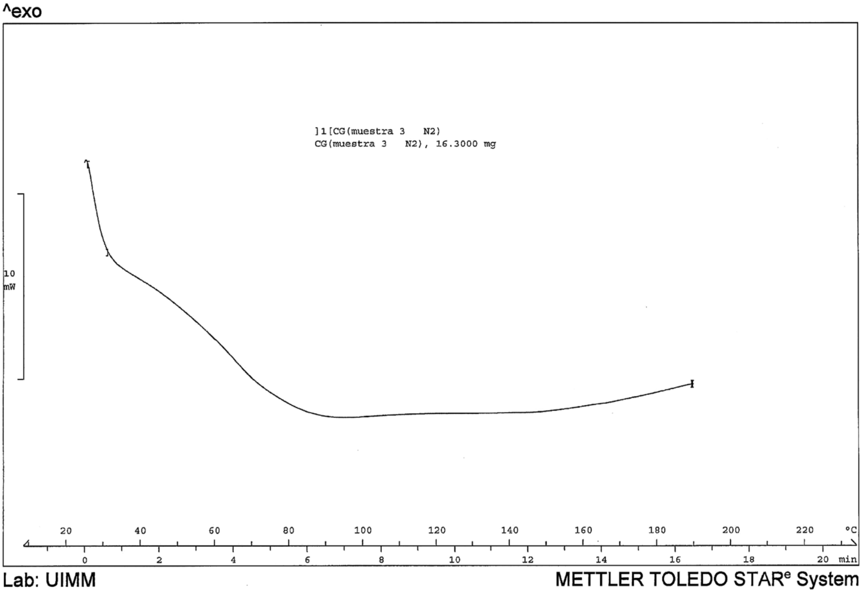

FIGURE 8 DSC scan obtained for mixture 3 (90% potato starch, 5% glycerol, 5% jute).

(20–200°C) for mixtures 2 and 3, corresponding to potato starch specimens reinforced with 5% of sisal and jute fibers, respectively. A partial broad endothermic peak similar to that shown in Figure 6 can be observed in both cases.

Thermogravimetry (TGA)

All processed biocomposite specimens showed similar tendencies in the TGA experiments, in particular under O_2 atmosphere (Figure 9). In all cases, major decomposition accompanied by a pronounced weight loss can be characterized by an inflection temperature. No considerable weight loss was observed in the usual range 20–100°C due to absorbed and bound water in the compression-molded specimens. As in ATR-IR spectroscopy, this might be due to the actual processing conditions used to prepare the specimens because unprocessed potato starch shows the typical weight loss shoulder-type peak due to bound water in the range 20–100°C as evidenced in Figure 9. Comparative measurements of moisture content of the unprocessed starch powders were obtained using a Mettler Toledo Moisture Anlayzer. Native potato, sweet potato, and corn starch powders showed moisture

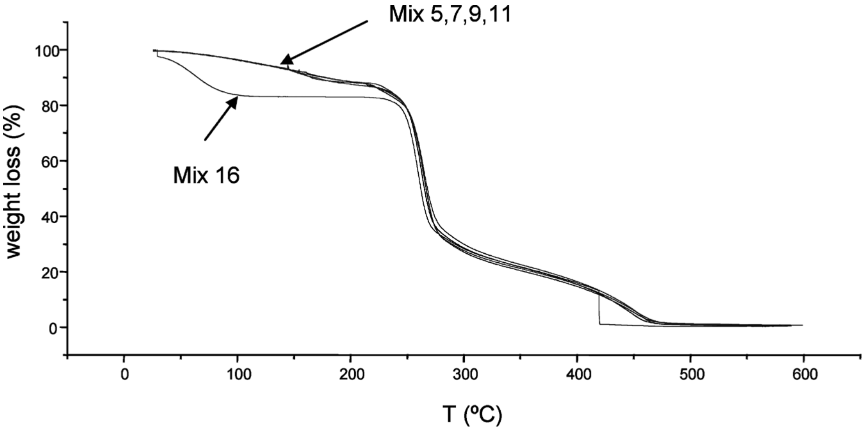

FIGURE 9 TGA curves for mixtures 5, 7, 9, and 11 from Table 1 and for unprocessed potato starch (mix. 16) with O_2 atmosphere.

contents of 22, 16, and 16%, respectively. Processed specimens displayed moisture contents in the order of 3–5%, after being exposed to an environment with a relative humidity of 80%.

The unreinforced specimens show an inflection point at lower temperatures (262°C) compared to the fiber reinforced specimens (266–277°C). Corn starch reinforced with 5% sisal fibers by weight showed similar inflection temperatures (271°C) with potato starch specimens with 5% sisal fibers (279°C). In general, the type of starch used did not show an important effect on the inflection temperature at which major decomposition and weight loss occurs.

In an O_2 atmosphere, all specimens show the same total weight loss (circa 100% in Figure 9). However, in an argon atmosphere (Figure 10), a variation of up to 10% in the total weight loss between the different specimens was found. The smallest weight loss (87%) was found for sample 7 (95% potato starch/5% chitin/0% fibers), whereas the greatest weight loss (98%) corresponded to sample 12 (90% corn starch/5% glycerol/5% sisal).

Morphological Characterization

Natural fiber reinforced starch biocomposites show some similar features compared to natural fiber reinforced thermoplastics [16]. However, depending on the type of fiber and type of plasticizer different structures were observed under the SEM. Figure 11 shows a typical fracture surface morphology for a natural fiber composite, in

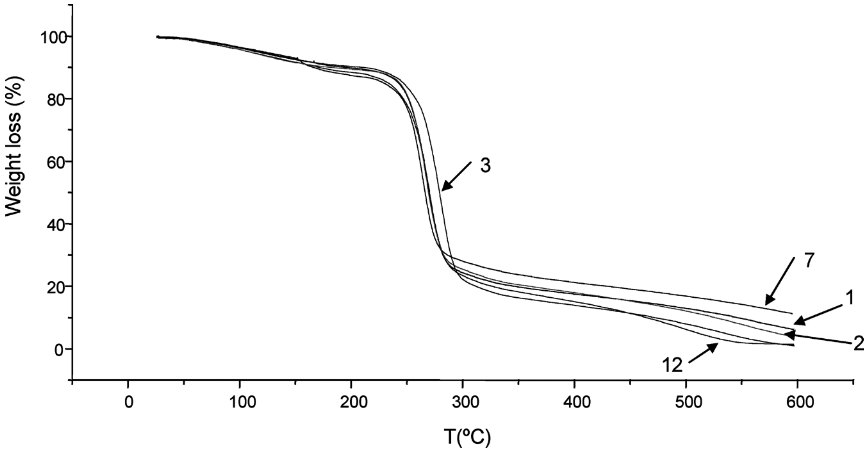

FIGURE 10 TGA curves for mixtures 1, 2, 3, 7, 12 from Table 1 with argon atmosphere.

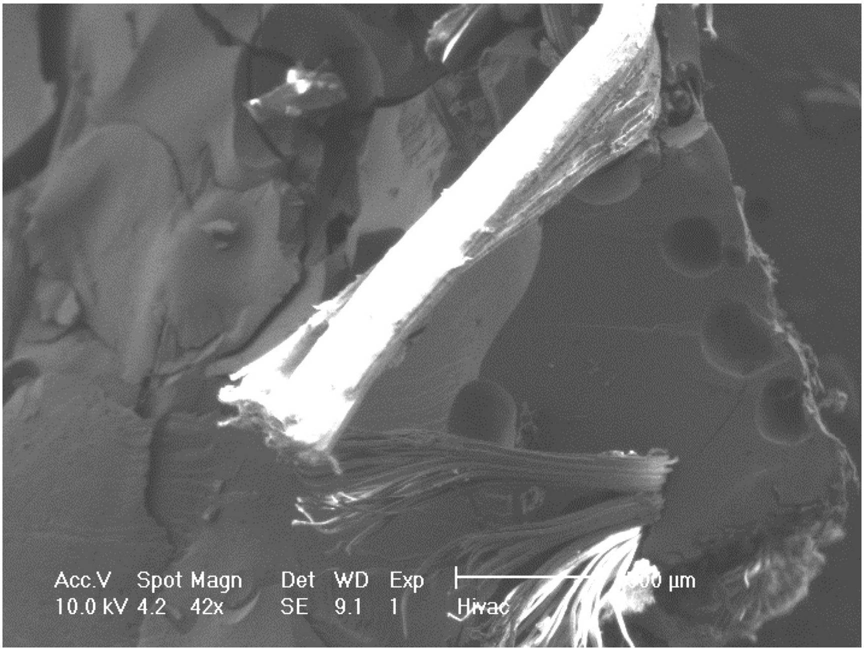

FIGURE 11 SEM picture of fractured specimen from mixture 4 (90% potato starch, 5%, sisal, and 5% water). The scale bar reads 500 µm.

this case with 90% potato starch and 5% of sisal, with 5% of water as plasticizer. Fiber defibrillation can be observed in one of the fibers. Several spherical voids about 200 μm in diameter can be observed in the starch matrix. In general terms, good adhesion can be observed between natural fibers and the starch matrix, especially if compared to natural fiber reinforced thermoplastics [15,19].

The surface morphology of an unreinforced potato starch (95%) and 5% water mixture can be observed in Figure 12. Voids with different types of shapes and dimensions varying from 5 to 50 μm can be seen in the matrix.

Figure 13 shows the surface of a composite with 5% sisal fiber reinforcement and matrix made out of blend of 95% of potato starch and 5% of chitosan solution. Several spherical voids with varying sizes can be observed in the matrix. This pattern occurs in a much larger scale in Figure 14, where the surface of an unreinforced starch-chitosan is displayed. In this case, spherical voids of varying dimensions can be observed over the whole domain. This is probably associated with the presence of the chitosan solution used as a plasticizer. During the

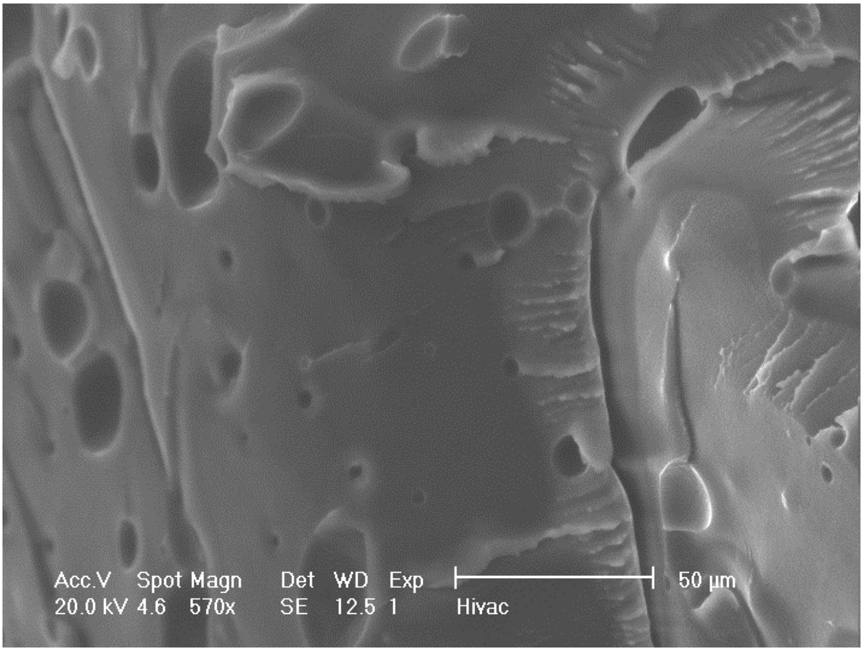

FIGURE 12 SEM picture of fractured specimen from mixture 5 (95% potato starch and 5% water).

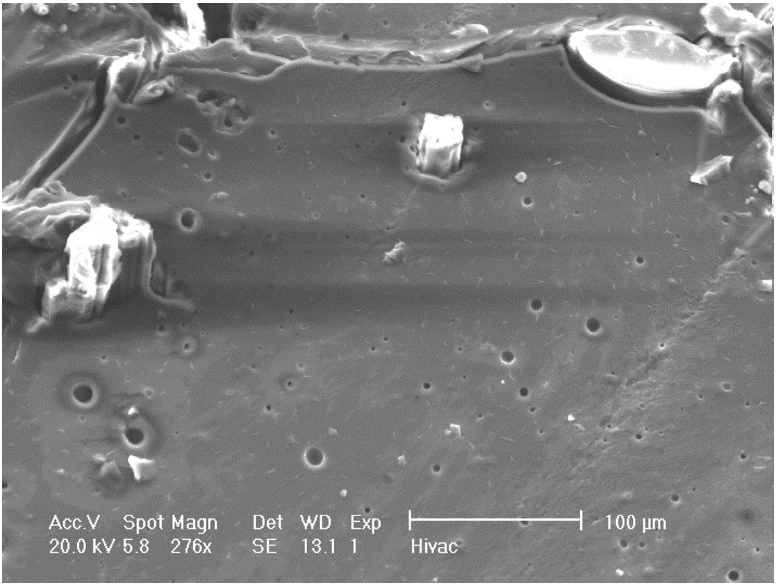

FIGURE 13 SEM picture of fractured specimen from mixture 6 (90% potato starch, 5% sisal, and 5% chitosan solution).

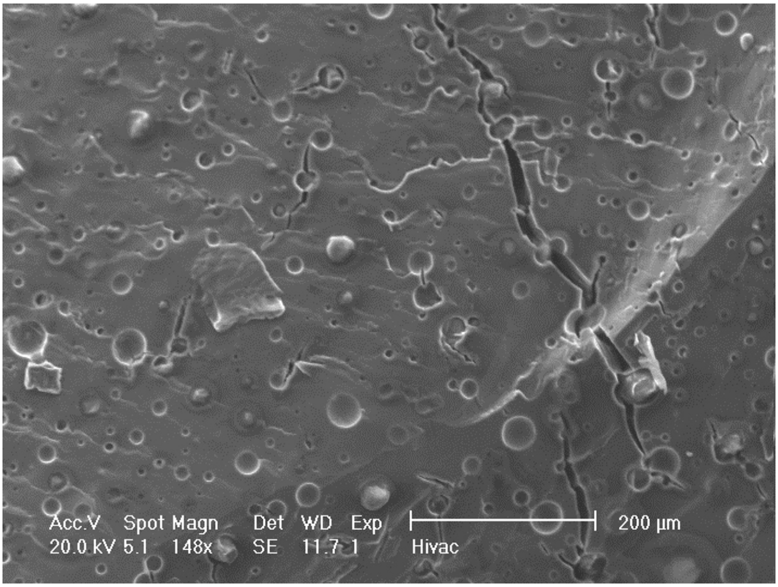

FIGURE 14 SEM picture of fractured specimen from mixture 7 (95% potato starch, 5% chitosan solution).

preparation of the specimens using the hot press, these bubbles might have been formed due to solvent evaporation.

CONCLUSIONS

Different techniques have been used to characterize the structure and thermal properties of natural fiber reinforced starch based biocomposites. ATR-IR analysis of the specimens showed that the different types of starch used have similar functionalities. In some cases the presence of fibers produced slightly different results from the unreinforced specimens.

TGA analysis showed that the different types of starch and natural fibers used in the experiments produced similar weight loss patterns in all cases. A major inflection point was found in most cases in the temperature range 260–270°C. Unprocessed starch samples showed higher water content than the compression molded specimens.

A broad endothermic peak was found for the starch based biocomposites in the DSC experiments. Unprocessed pure starch specimens also showed a similar type of peak.

Morphological examination of the biocomposites showed that in most cases voids of different shapes and sizes are a typical feature. A more homogenous morphology was observed for water-plasticized specimens than for the cases where chitosan was used.

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