Development of Biodegradable Composites with Treated and Compatibilized Lignocellulosic Fibers

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ABSTRACT: The aliphatic polyester Bionolle 3020 was combined with lignocellulosic fibers, namely, flax, hemp, and wood, to produce biodegradable composite materials. The effect of two fiber surface treatments, acetylation and propionylation, and the addition of maleic anhydride (MA)-grafted Bionolle 3001 as a compatibilizer on the fiber/matrix interfacial adhesion was studied. The compatibilizer was synthesized through a MA grafting reaction in the presence of dicumyl peroxide as an initiator. The composites' mechanical properties, water absorption, fracture morphology (scanning electron microscopy), and biodegradation were evaluated. Both the fiber treatments and the compatibilizer incorporation significantly improved the composites' tensile strength, whereas an important reduction in the water absorption was found with the addition of treated fibers. Moreover, fiber incorporation into the matrix increased its biodegradation rate. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4703–4710, 2006

Key words: biodegradable; composites; mechanical properties

INTRODUCTION

The nonbiodegradability of most plastics is the cause of many environmental problems associated with their disposal. This situation leads to the increasingly difficult problem of finding available landfill areas for this waste.[1] A sufficient solution for this problem could be the development of fully environmentally friendly composites that consist of a biodegradable polymeric matrix and lignocellulosic natural fibers. Biodegradable polymers constitute a loosely defined family of polymers that are designed to degrade through the action of living organisms.[2,3] Typical biodegradable polymers that are commercially available include polycaprolactone (PCL), poly(lactic acid), polyhydroxyalkanoates, poly(ethylene glycol), and aliphatic polyesters, such as poly(butylene succinate) and poly(butylene succinate-*co*-butylene adipate).[2,3] In addition, lignocellulosic materials appear to be a suitable filler or reinforcing agent for biodegradable matrices; these exhibit attractive properties, such as low density, low cost, abundance, renewability, and biodegradability.[4–7] Recently, the incorporation of lignocellulosic materials in biodegradable matrices has become the subject of considerable research. Shibata et al.[8] and Avella et al.[9] studied the mechanical properties of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) composites reinforced with short abaca and wheat-straw fibers, respectively. Dufresne et al.[10] evaluated the effect of residual lignocellulosic flour from spruce and ground olive stone in composites based on poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate). Mohanty et al.[11,12] studied the influence of the surface modification of jute fibers on the performance of biodegradable jute/biopol[11] and jute/polyester amide composites.[12] In addition, Nitz et al.[13] evaluated the addition of wood flour and lignin in PCL and the compatibilization of these composites with PCL-*g*-maleic anhydride (MA). Plackett et al.[14] investigated jute fiber incorporation in ʟ-polylactide. Franco et al.[15] evaluated the susceptibility of sisal-fiber-reinforced PCL/starch blends to different degrading environments. Gatenholm et al.[16] investigated the properties of composites made from bacteria-produced polyesters reinforced with wood cellulose. Le Digabel et al.[17] studied the properties of biodegradable composites based on wheat-straw lignocellulosic fillers. Soykeabkaew et al.[18] and Averous and Boquillon[19] investigated biocomposite-based plasticized starch and agromaterials. However, there were only two studies, one by Wollerdorfer and Bader[20] and one by Baiardo et al.,[21] concerning the use of poly(butylene succinate-*co*-butylene adipate) polyester as a matrix for com-

posite production. Wollerdorfer et al.[20] studied the influence of different grades of natural fibers on the mechanical properties of the composites. They used flax, ramie, jute, oil palm, and cellulose fibers in combination with the polyester Bionolle 3020, polysaccharides, and blends of cornstarch with biodegradable polymers. Baiardo et al.[21] investigated the effect of fiber treatment with different chlorides on the properties of flax fiber/Bionolle 3020 composites.

The main disadvantage encountered during the incorporation of natural lignocellulosic materials into polymers is the lack of good interfacial adhesion between the two components, which results in poor properties in the final material.[22] Polar hydroxyl groups on the surface of the lignocellulosic materials have difficulty forming a well-bonded interface with a nonpolar matrix, as the hydrogen bonds of the fiber surface tend to prevent the wetting of the filler surfaces. Furthermore, the incorporation of lignocellulosic materials in synthetic polymers is often associated with agglomeration as a result of insufficient dispersion, caused by the tendency of the fillers to form hydrogen bonds with each other. Therefore, to develop such composites with good properties, it is necessary to decrease the hydrophilicity of the lignocellulosic materials by chemical modification or to promote interfacial adhesion through the use of a compatibilizer. The chemical modification is usually obtained through the use of reagents having functional groups that are capable of bonding to the hydroxyl groups of the lignocellulosic materials. Chemical treatments, such as dewaxing, acetylation, and chemical grafting, are used to modify the surface properties of the fibers.[23–28] Another effective way to improve the interface between the fiber and matrix is to use compatibilizers, which are usually graft copolymers of a polymeric matrix, and an anhydride such as MA.[29–31] These reagents are compatible with the polymeric matrix and also can react with the hydroxyl groups of the fiber, forming covalent bonds. Both methods, modification of the lignocellulosic materials and the use of compatibilizers, improve the stress transfer between the two components and lead to the improvement of the mechanical and physical properties of the produced composites.

The aim of this study was the production of green polyester composites reinforced with different lignocellulosic fibers, including as flax, hemp, and wood fibers. In a previous work,[32] fiber surface treatments by means of acetylation and propionylation were evaluated. In this study, the effects of fiber surface treatments and compatibilizer addition on the composite hydrophilicity, mechanical properties, and biodegradation were investigated.

EXPERIMENTAL

Materials

The commercial polyesters Bionolle 3020 and 3001 were purchased from Showa Highpolymer Co., Ltd. (Tokyo). The two polyesters had the same structure, as they were copolymers of succinic and adipic dimethylesters with 1,4 butanediol, and they differed only in terms of molecular weight.[33] The number-average molecular weights of Bionolle 3020 and Bionolle 3001 were 72,500 and 101,300, respectively. Three different natural fibers were used in this study. Flax and hemp fibers were purchased from S. A. Van Robaeys Frères (Killem, France), and wood fibers (*Pinus silvestris*) from WKI (Braunschweig, Germany). MA (99%; Aldrich, Germany), dicumyl peroxide (98%; Aldrich, Germany), and chloroform (Riedel-de-Haen, Germany) were used as received.

Fiber treatment and characterization

The treatment of the fibers with acetic and propionic anhydride and the characterization of the untreated and esterified fibers were described extensively in a previous study.[32] Because the ester content of the treated fibers did not change significantly after 2 h of reaction time at 120°C, we chose to use these conditions for the esterification of the materials.

Preparation and characterization of the compatibilizer

The grafting reaction and the compatibilizer characterization were described in previous studies.[33–35] The graft content and the viscosity of the compatibilizer that was used in this study were determined via titration and an Ubbelohde viscometer (Mainz, Germany) and were found to be 1.81 wt % and 0.75 dL/g, respectively.

Preparation of the composites

The fibers and the polymer Bionolle 3020 were mixed in a Haake Buchler (Germany) rheomixer. Before mixing, the fibers were dried in a vacuum oven at 75°C for 24 h to prevent the formation of porous products by water evaporation during the composite preparation. The fiber content in the composites was 30 wt %. Blending was performed at 130°C for 10 min at a rotor speed of 20 rpm. The amount of the compatibilizer was 5 wt %.

Characterization of the composites

Mechanical properties

Tensile strength, Young's modulus, and elongation were measured on a Zwick (Ulm, Germany) mechan-

Tensile strength at yield (MPa)	23.5 ($\pm$0.7)
Tensile strength at break (MPa)	26.1 ($\pm$0.6)
Elongation at yield (%)	22.2 ($\pm$2.4)
Elongation at break (%)	520 ($\pm$60)
Modulus of elasticity (MPa)	375 ($\pm$40)

ical tester (model 1445) according to ASTM D 638. The samples were prepared in a hydraulic press at 140°C. The crosshead speed during the testing was 5 mm/min. Six measurements were conducted for each sample, and the results were averaged to obtain a mean value.

Before mechanical measurements, the samples were conditioned at 50 ± 5% relative humidity for 48 h at ambient temperature in a closed chamber containing a saturated H_2SO_4 solution in distilled water (ASTM E 104).

Water absorption

Water absorption was determined according to ASTM D 570. The samples were first soaked in distilled water. At regular time intervals, each sample was removed from the water tank, dried by wiping with a blotting article, and subsequently weighed to determine the water uptake. The samples were placed back in water after each measurement. The water absorption was calculated as the weight difference and is reported as the percentage increase of the initial weight.

Biodegradation

The biodegradation of the specimens was performed according to ISO 846. Specimens with dimensions 30 × 30 × 1 mm prepared in a hydraulic press at 140°C were buried in soil for 1, 3, and 5 months.

Scanning electron microscopy (SEM)

The fracture surface of the composites and the effect of biodegradation on the composite surface was examined with a SEM microscope (LEO 435VP, Germany). Before the analysis, the samples were coated with gold (~30 nm) to prevent sample charging under the electron beam.

RESULTS AND DISCUSSION

Characterization of the composites

Mechanical properties

In Tables I–III, the mechanical properties of the matrix and composites containing 30 wt % lignocellulosic fibers are shown. As shown, the addition of lignocellulosic fibers into the polymeric matrix resulted in a significant change in its mechanical properties. In particular, the fiber addition led to a slight decrease in the tensile strength from 26.1 MPa for Bionolle 3020 to 25.4 MPa for flax composites, 23.2 MPa for hemp composites, and 20.2 MPa for wood fiber composites. For the Young's modulus values, an increase from 375 MPa for Bionolle 3020 to 1580 MPa for flax composites, 1520 MPa for hemp composites, and 1420 MPa for wood fiber composites was observed. Moreover, in the case of elongation at break, a significant reduction from 520% for Bionolle 3020 to 2–3% for the composites was observed.

The decrease in the tensile strength with fiber addition (Table II) was expected and has been reported in other studies.[36–38] This was mainly attributed to the weak interfacial adhesion between the nonpolar polymeric matrix and the polar lignocellulosic fibers, which promoted microcrack formation at the interface and led to premature failure.[39]

From Table II, it is also clear that the reduction of material tensile strength with fiber incorporation was higher for wood fibers (a 22.6% decrease) and lower for flax (2.7%) and hemp (11.1%) fibers, respectively. The fact that flax and hemp lignocellulosic materials were fibrous, whereas wood was flakelike with an irregular shape and size, could provide an explanation for the observed difference. It is known from the literature that fibers were more effective compared to other reinforcing agents due to their geometric characteristics (aspect ratio).

As already mentioned, one of the most important factors affecting the mechanical properties of the composites was the degree of adhesion between its components. Thus, to develop composites with sufficiently

TABLE II
Tensile Strength of the Composites

Fiber	Tensile strength at break (MPa)			
	Untreated	Acetylated	Propionylated	With compatibilizer
Flax	25.4 ($\pm$0.9)	28.6 ($\pm$0.6)	29.4 ($\pm$0.6)	33.3 ($\pm$1.0)
Hemp	23.2 ($\pm$0.6)	26.1 ($\pm$0.5)	25.4 ($\pm$0.5)	29.6 ($\pm$0.4)
Wood	20.2 ($\pm$0.8)	24.6 ($\pm$0.5)	24.4 ($\pm$0.7)	27.3 ($\pm$1.0)

TABLE III
Young's Modulus of the Composites

Fiber	Young's modulus (MPa)			
	Untreated	Acetylated	Propionylated	With compatibilizer
Flax	1580 (±60)	1610 (±60)	1610 (±30)	1720 (±40)
Hemp	1520 (±50)	1560 (±40)	1520 (±50)	1700 (±40)
Wood	1420 (±40)	1500 (±40)	1520 (±60)	1610 (±50)

good mechanical properties, the fiber/matrix interfacial adhesion was promoted by means of fiber treatments, that is, acetylation and propionylation, and the addition of MA-grafted Bionolle 3001 as a compatibilizer.

As shown in Table II, acetylation and propionylation resulted in a material with a higher tensile strength. It appeared that the substitution of the hydrophilic hydroxyl groups of the lignocellulosic material with acetyl and propionyl groups rendered the lignocellulosic fiber surface more hydrophobic[23] and thus more compatible with the hydrophobic polymeric matrix, which led to a material with improved properties. However, this improvement, ranging from about 10 to 22%, was not high enough compared to those obtained with the compatibilizer addition, which varied from about 28 to 35%. More specifically, for flax, hemp, and wood fiber composites, the addition of 5 wt % compatibilizer increased the tensile strength from 25.4 to 33.3 MPa, 23.2 to 29.6 MPa, and 20.2 to 27.3 MPa, respectively, values higher than that of the pure matrix (26.1 MPa). The excellent performance of Bionolle 3001-g-MA as a compatibilizer in the fiber/polymeric matrix composites was attributed to the following two factors: (1) the ability of the MA to react with the hydroxyls of the fibers and (2) the enhanced compatibility of the grafted copolymer chains with the main polymeric phase.

Table III shows that fiber incorporation in the polymeric matrix significantly increased the stiffness of the produced materials and resulted in Young's modulus values between 1420 and 1580 MPa, as compared to 375 MPa in the pure matrix. Fiber surface esterification and compatibilizer addition did not have a significant effect on Young's modulus and led to a marginal improvement, which was more pronounced with compatibilizer addition.
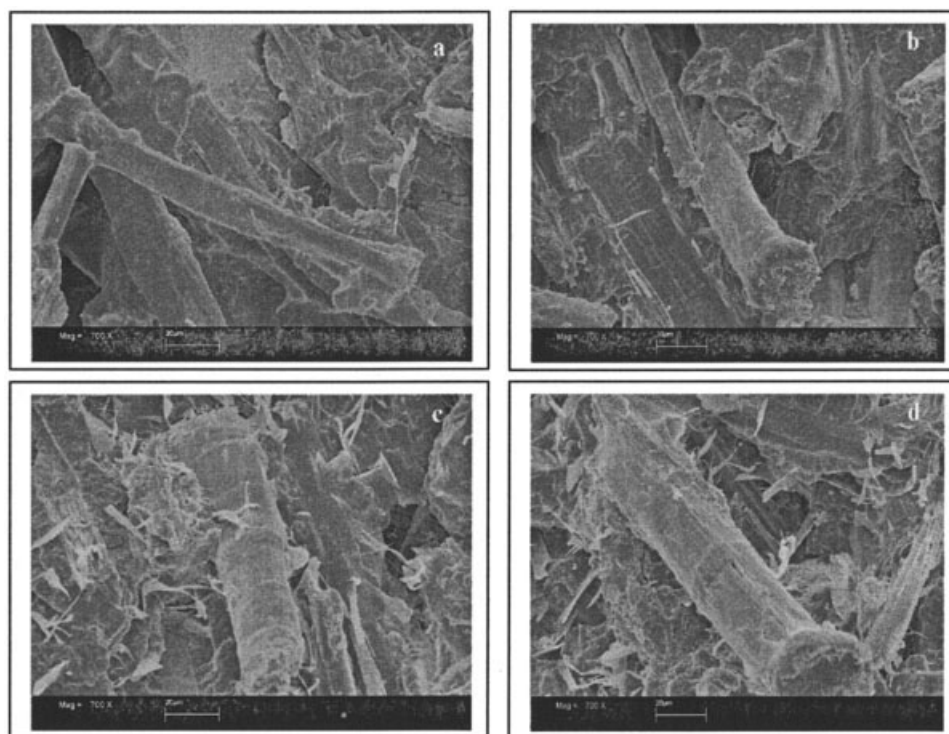

Figure 1 SEM micrographs of the fracture surfaces of the composites: (a) untreated, (b) acetylated, (c) with propionylated flax fibers, and (d) with compatibilizer addition.
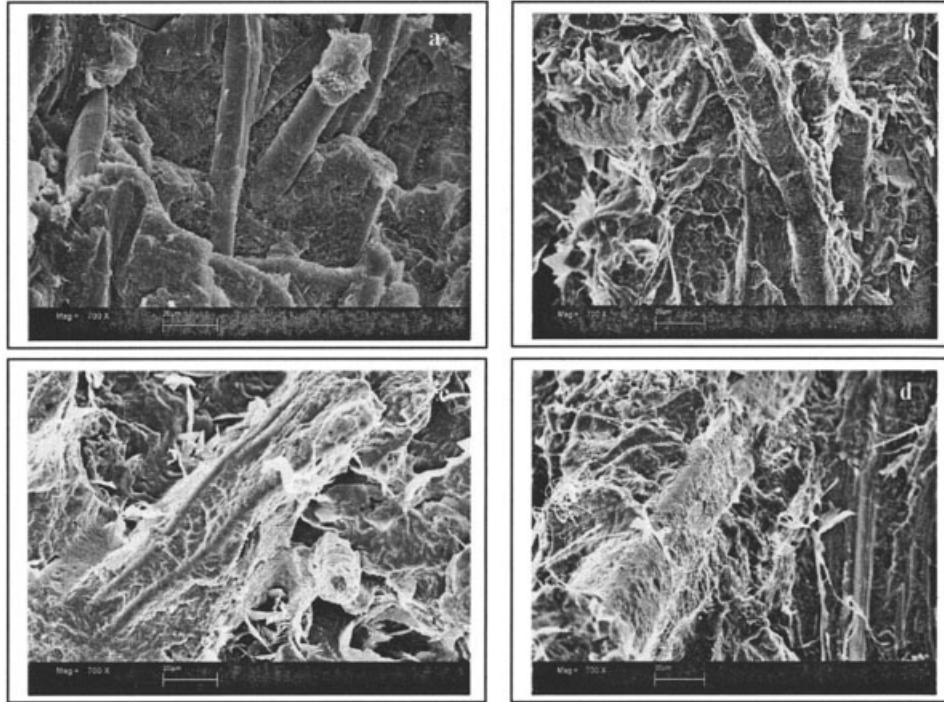
Figure 2 SEM micrographs of the fracture surfaces of the composites: (a) untreated, (b) acetylated, (c) with propionylated hemp fibers, and (d) with compatibilizer addition.

Interfacial properties

The state of the fiber/matrix interface was investigated with SEM. In Figures 1–3 are given the SEM micrographs of the fracture surfaces of the three composites. As seen, microscopy revealed that there was a remarkable difference in the fiber/matrix interaction
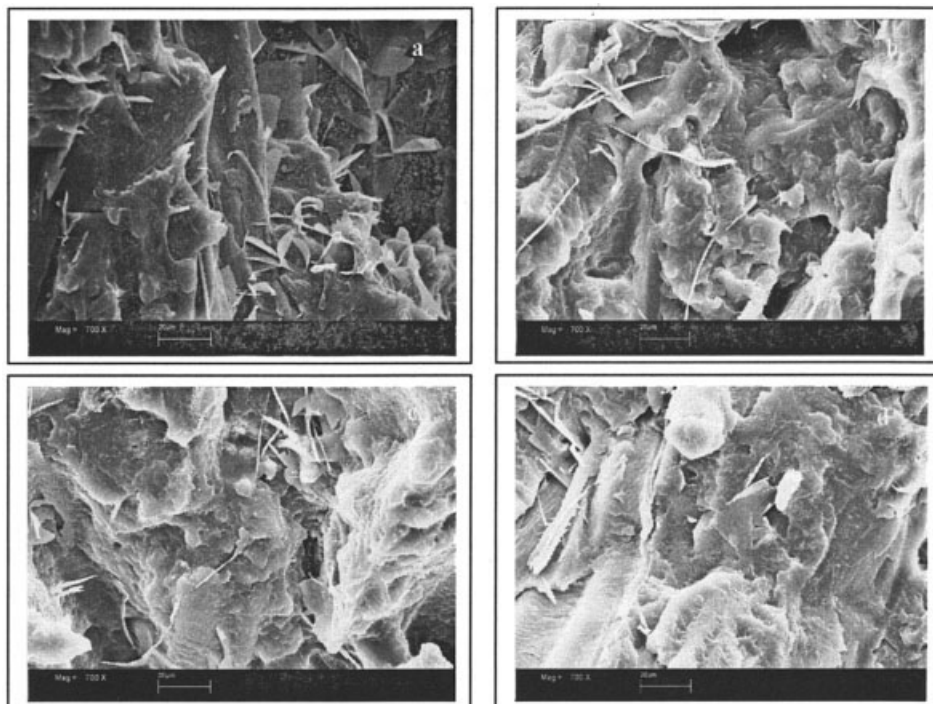

Figure 3 SEM micrographs of the fracture surfaces of the composites: (a) untreated, (b) acetylated, (c) with propionylated wood fibers, and (d) with compatibilizer addition.
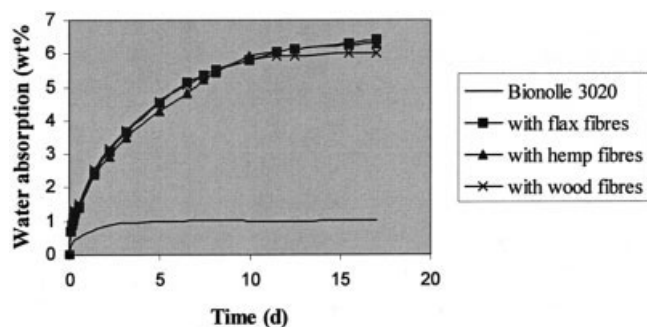
Figure 4 Water absorption curves of the polyester and composites containing untreated (a) flax, (b) hemp, and (c) wood fibers (d = days).

between the untreated fiber, the esterified fiber, and the compatibilized composites. Composites containing esterified fibers and compatibilizer showed better fiber dispersion, a more effective fiber wetting by the matrix, and improved adhesion between the two phases.

As seen on the surface of untreated fibers [Figs. 1–3(a)], there was only weak matrix adhesion, in contrast to that on the surface of the treated and compatibilized fibers [Figs. 1–3(b,c,d)], which were covered by layers of matrix material being pulled out together with the fibers from the matrix. This suggested that in composites prepared with untreated fibers, failure occurred at the fiber/matrix interface as a result of the poor interfacial adhesion existing between the fiber and the matrix, whereas in composites prepared with treated and compatibilized fibers, failure increasingly occurred within the matrix.

Water absorption

It is known that lignocellulosic-based composites absorb water and cause undesirable dimensional changes in the final product.[40] In addition, water absorption may cause rapid debonding, delamination, and a loss of structural integrity,[41] which leads to the deterioration of the material's mechanical properties. As the immersion time of the composite in water increases, the composite tensile strength decreases.[42] In water-immersion experiments, the extent of water uptake by composites depends strongly on the amount and nature of the fibers and the matrix. Thus, for composites containing lignocellulosic materials such as flax, hemp, and wood fibers, an increase in the water absorption is expected, as compared to composites made with ceramic or polymer fibers.

In Figure 4 is given the variation of water uptake with the immersion time of the composites containing untreated flax, hemp, and wood fibers. As shown, the weight increase of the composites depended on exposure time. A rapid water absorption was observed for

all of the samples during the first days of immersion, which decreased gradually afterward and reached a plateau. The hydrophilic nature of the fibers was confirmed by the fact that all of the composite materials absorbed six times more water than the matrix.

In addition, the effect of fiber treatment and compatibilizer addition on composite hydrophilicity was studied, and the results are shown in Figure 5.

Undoubtedly, the fiber treatments led to a significant reduction in the composite water uptake. As seen in Figure 5, composites containing treated fibers absorbed almost half the amount of water as compared to those containing untreated fibers. This fact could be attributed to the substitution of hydrophilic hydroxyl groups of the lignocellulosic fibers with acetyl and propionyl groups, which rendered the lignocellulosic fiber surface more hydrophobic,[32] and thus, when these fibers were introduced in the polymeric matrix, a less hydrophilic material was produced.

In the case of compatibilizer addition, a reduction in water uptake was also observed, but as shown in Figure 5, it was much lower than that observed for the treated fibers. For compatibilizer addition, the water absorption reduction was attributed to the formation of covalent bonds between the functional groups of MA and the hydroxyl groups at the fiber surface,[43] whereas for fiber treatments, as already explained, it was attributed to hydroxyl group substitution by acetyl and propionyl groups. Thus, on the basis of the water uptake reduction data, we also concluded that the number of hydroxyls forming covalent bonds was much lower than that reacting with acetic/propionic anhydride.

Biodegradation

To investigate the biodegradability of the produced composites, soil burial degradation was carried out for 1, 3, and 5 months. The photographs of the remaining sample composites after different degradation periods are presented in Figure 6. The photographs of the
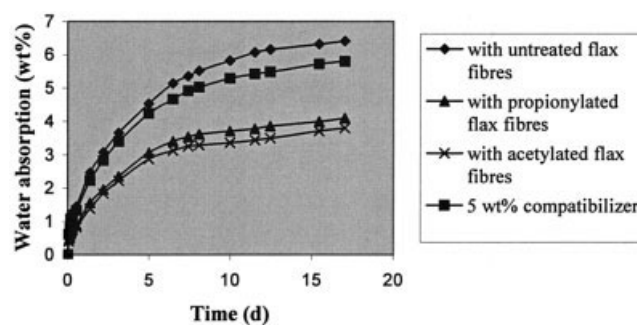

Figure 5 Water absorption curves of untreated composites, acetylated composites, composites with propionylated flax fibers, and composites with compatibilizer addition (d = days).
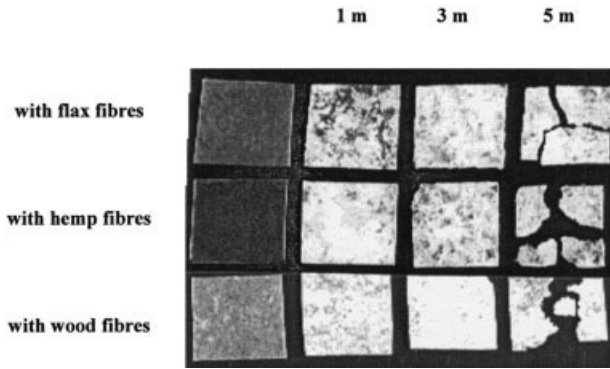
1 m   3 m   5 m

with flax fibres

with hemp fibres

with wood fibres

Figure 6 Photographs of the composites showing the progression of biodegradation with time (m = months).

remaining samples of the pure matrix were already been shown in a previous study.[33] Sample biodegradation was easily observed after about 1 month of soil burial and kept rapidly increasing with time.

The fast degradation could be explained by the fact that lignocellulosic fibers, which are highly hydrophilic, transferred water into the composite by means of capillary phenomena[40] and thus sped up the degradation process. Moreover, the humid environment promoted the growth of microorganisms, and consequently, the hydrolysis of the ester groups of the polyester increased. After 1 month of biodegradation, the composite surface was discolored from brown to white. The biodegraded composites appeared to be heterogeneously eroded and exhibited an irregular surface with many holes of different sizes and depths. Afterward, at 3 and 5 months, biodegradation took place to a greater extent, and finally, the samples were
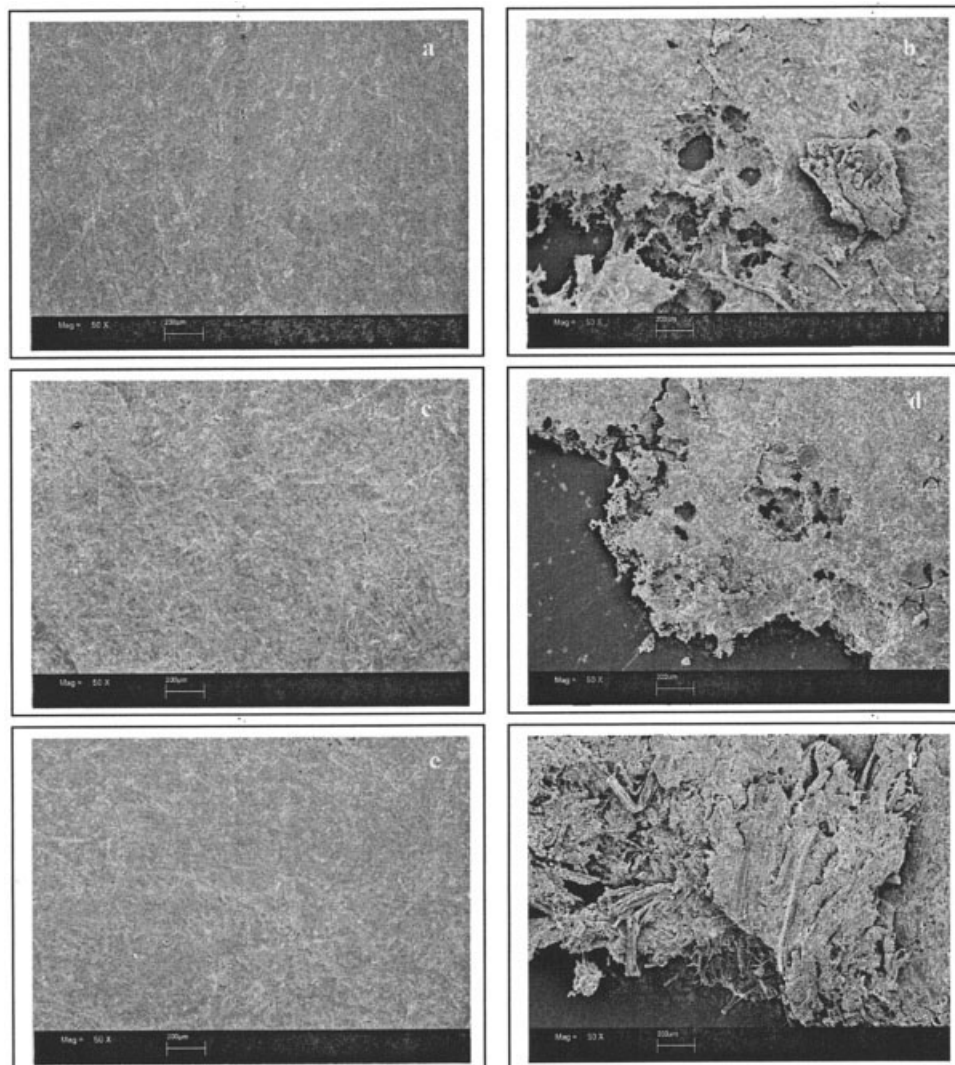

Figure 7 SEM micrographs of the composites before degradation with (a) flax, (c) hemp, and (e) wood fibers and of the composites 5 months biodegradation with (b) flax, (d) hemp, and (f) wood fibers.

completely damaged by the microorganisms. This was more pronounced after 5 months, as shown in Figure 7, where the SEM micrographs of the three composites after 5 months of degradation are given. According to the micrographs, there was significant corrosion of the composite surface, indicating microorganism attack.

CONCLUSIONS

The results of this study could be summarized as follows:

1. The incorporation of lignocellulosic fibers into the polymer reduced the matrix tensile strength and significantly increased its tensile modulus, water absorption, and biodegradation rate.
2. Acetic/propionic anhydride treatment of the fibers, although it was not proven to be a very effective method for improving the matrix tensile strength, significantly reduced the water uptake, as composites containing treated fibers absorbed half the amount of water compared to those containing untreated fibers.
3. The use of the Bionolle 3001-*g*-MA compatibilizer significantly improved the mechanical properties of the composites and especially their tensile strength.

Thus, with a suitable combination of fiber grade and composition and the interfacial adhesion improvement method, one can produce composites with a controlled biodegradation rate, hydrophilicity, and mechanical properties.

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