Composites of Poly(lactic acid) with Flax Fibers Modified by Interstitial Polymerization

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ABSTRACT: Natural fiber composites were designed and optimized to achieve good mechanical properties and resistance to growth of living organisms. Composite materials were prepared from poly(lactic acid) (PLA) with flax fibers, which had been subjected to interstitial polymerization to replace the water in the cellulose fibers. Prior to the polymerization, the flax fibers were extracted with sodium hydroxide and acetone to remove lignin, pectin, and waxes from the cellulose. Differential scanning calorimetry was used to study the crystallization and melting of the composites compared to pure PLA. The surface wetting of the fibers and morphology of the composites were studied by scanning electron microscopy and optical microscopy. Mechanical properties were studied using dynamic mechanical analysis. The influence of the interstitial polymerization on the dynamic storage modulus was found to be significant. The composites of polymerization treated flax with acetone washed fibers had higher storage moduli than the unwashed fiber composites, which suggested that the adhesion between the flax fibers and the matrix was improved by the treatments. The composites were subjected to moist environmental conditions in order to test for development of mold and fungi, and the acetone washed polymerization treated flax composites were resistant to these growths. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3620–3629, 2006

Key words: composites; fibers; biodegradable; graft copolymers; polyesters

INTRODUCTION

The use of biodegradable polymers with natural fibers for composite applications has created renewed interest in the past decade as substitutes for glass fiber composites. The reasons for the shift have been mainly due to suitable performance, economic, ecological, and social reasons. As a result of many government regulations and increased environmental awareness, there is a growing desire for application of renewable resources.[1–3] In order to preserve their environmental and ecological advantages, natural fibers should be used in composites with either biodegradable or recyclable polymers, preferably thermoplastics.

Flax is a natural fiber that is being used in composite applications. Flax fibers are contained in fiber bundles in a layer of the bark referred to as the "bast" layer. The individual fibers or filaments are made of cellulose and hemicellulose and are bonded together by some form of matrix, which can be lignin or pectin. There are several advantages of using natural fibers, such as flax, hemp, or jute, when compared with glass fibers[1]:

- natural fibers have similar specific modulus and strength to glass fibers, after allowing for differences in density;
- natural fibers are a readily renewable resource;
- natural fibers are biodegradable and thus have a lower impact on the environment; and
- natural fibers have lower cost than traditional glass fibers.

Natural fiber composites have many advantages over glass fiber composites, depending on the application. The advantages can be viewed in terms of lower density that results in higher specific strength and stiffness, easier processing, no tooling wear, and the possibility of thermal recycling. Possible disadvantages are lower absolute strength and stiffness (particularly impact strength), variable fiber quality, moisture absorption that causes swelling of the fibers, and durability of the composites.[4] These properties need to be improved in order to achieve the optimum benefits of natural fibers as a substitute for the existing glass fiber composites.

Poly(lactic acid) (PLA) is a biodegradable polymer produced from renewable resources by the ring-open-

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ing polymerization of lactides, in which the lactic acid monomers are obtained from the fermentation of sugar feed stocks.[5] A recent study by Andreopoulos[6] showed that, although PLA is inherently brittle, it can be modified by plasticizers[7,8] that significantly improve the mechanical properties and processability of the composites. PLA has a melting temperature of 170°C, which is similar to polypropylene, a thermoplastic typically used in natural fiber composites. The polar structure of PLA is expected to provide improved fiber–matrix bonding and hence improved composite properties.[9]

Interstitial polymerization (IP) has been used with synthetic polymers[10] for improvement of mechanical properties. The concept of IP has not been reported for use in natural fibers, although it represents a simple solution to many problems associated with durability and properties of natural fibers. The purpose of IP in this research is to replace water, which is naturally present in up to 10% in cellulose fibers. It is designed to eliminate processing difficulties and disadvantages that occur when water and organic materials are combined. This results in conditions for growth of mold and fungi; steaming during molding and melting processes; shrinkage that occurs when water evaporates; and loss of water during processing, which causes friability of natural fibers. All of these properties are expected to be reduced when the water is replaced.[11] A solution to this problem that has been explored is to replace the water in the fibers with a high boiling temperature plasticizer, such as tributyl citrate.[12] If water is replaced by monomers penetrating the tubular cellulose fibers interstitially, the fiber volume fraction can effectively be preserved when the absorbed monomer is polymerized. Thermal and mechanical properties can be stabilized and the fibers protected from environmental conditions. IP in natural fibers was used with several acrylate monomers in order to tailor the softening temperature of the interstitial polymer and to provide good mechanical properties over a wide temperature range.

The Fox equation was used to calculate the relative proportion of comonomers that were to be polymerized within the flax fibers. The polymer glass-transition temperature, also known as the softening temperature, of a mixture of two compounds (monomers) can be defined by the Fox equation[13] as follows:

$$\frac{1}{T_g}=\frac{\omega_1}{T_{g_1}}+\frac{\omega_2}{T_{g_2}} \tag{1}$$

where ω_1 and ω_2 are the respective weight fractions of monomers 1 and 2 and T_{g_1} and T_{g_2} are the respective glass-transition temperatures of each monomer.

The objective was to modify flax fibers internally through absorption and polymerization of acrylate monomers into purified and dried flax fibers. This causes the water that is normally present to be replaced by the acrylate polymer. The modified fibers were expected to provide relatively constant properties under variable humidity, to resist mold growth, and to be more stable under the elevated temperatures required for compression molding of thermoplastic composites. PLA was chosen as the matrix thermoplastic because it has a suitable melting temperature, it is derived from renewable materials, and it is biodegradable. Polypropylene is also a suitable polymer for preparation of these composites because it can be molded in the temperature range where flax fibers are stable, although under normal conditions such composites can lose an indeterminate amount of water that will result in lack of control of properties.[14]

EXPERIMENTAL

Materials

Durafiber flax grade 1 fiber (95% purity) was supplied by Cargill Inc. All fibers were dried in a vacuum oven at 60°C for 3 h to remove moisture. PLA (number-average molecular weight = 20,000 g/mol) was dissolved in chloroform before being mixed with natural fibers.

The initiator used for polymerization reactions was azobisisobutyronitrile (AIBN, Eastman). Different monomers, such as butyl acrylate (BA, BDH Laboratory Supplies), 2-ethylhexyl acrylate (EHA, Aldrich Chemical Company Inc.), and methyl methacrylate (MMA, BDH Laboratory Supplies), were used for the absorption and polymerization. A crosslinking monomer, ethylene dimethacrylate (Monomer–Polymer Laboratories Inc.), was only used during initial polymerizations, because the crosslinking prevented the polymer from being washed from the outside of the treated flax fibers.

Pretreatment of flax fibers

The flax fibers were subjected to a series of treatments before subsequent polymerization. They were subjected to Soxhlet extraction with acetone to remove any waxes that were present. The fibers were then washed in sodium hydroxide (2 mol/L) at 30°C for approximately 1 h to remove lignin associated with the flax. The sodium hydroxide solution was decanted and the fibers were washed in water, then washed in distilled water several times, and dried in air at room temperature. The washed flax fibers were placed in a vacuum oven at 60°C for 3 h to remove residual moisture.

Polymerization

Dried flax fibers were placed in a test tube with a vacuum side arm and an addition funnel. Specific monomers or monomer mixtures were added via the addition funnel with dissolved AIBN initiator (2 wt %). While the system was under vacuum, the monomer mixture was added to completely cover the flax. The vacuum was slowly released to atmospheric pressure to allow the monomer mixture to be forced to permeate into voids in the flax by atmospheric pressure. The immersed flax fibers were allowed to absorb the monomer mixture for 3–4 h in the sealed test tube. The fibers were removed from the test tube and, after absorption of the excess monomer mixture onto filter paper, the monomer absorbed flax fibers were placed in a sealed tube and warmed to 50°C in a water bath for 2 h to allow polymerization to proceed. The fibers were left overnight to complete the reaction. The reaction tubes were opened and heated to 100°C in a steam bath for 30 min to evaporate any residual monomer. The fibers were further dried in a vacuum oven at 60°C for at least 3 h, after which they were immersed in acetone for 15 min to remove any excess polyacrylate from their surface and then placed in a vacuum oven at 60°C for 3 h. The aim was to form the polymer only in the voids in the flax, not on the flax surface. It was expected that some grafting of the monomers onto the flax would occur, but this was not essential to the method. The goal was to absorb an amount of monomer similar to that of the water previously present in the flax, not to maximize the yield of grafting to the flax. Ethylene dimethacrylate was initially used to crosslink the polymer, but the polymer that formed on the outside of the flax could not be extracted. The crosslinking was found to be unimportant for the desired properties of the interstitial polymer. The T_g of the interstitial polymer was important, and this was achieved by using monomer compositions calculated using the Fox equation with BA or EHA as soft monomers and MMA as the hard monomer.

Preparation of composites

A known mass of polymer (PLA) was dissolved in a minimal amount of chloroform under reflux (15–20 mL/g) in order to intimately mix small amounts of flax and polymer. For larger samples, melt mixing was sufficient to provide a good composite and chloroform was not needed. Flax fibers at a fiber/polymer ratio of 1 : 1 (v/v) were mixed with the polymer solution and the solvent was allowed to evaporate initially under ambient conditions. The fibers were then dried in a vacuum oven at 60°C for 3 h to remove any remaining solvent. The fiber composite was cut into small pieces and pressed into a sheet between Teflon sheets using a heated press at a temperature between 173 and 176°C. No pressure was applied for 5 min and then 3-tonne pressure was applied for 5 min. The composite was also pressed into a rectangular bar under the same conditions, using a Teflon sheet as a spacer to obtain test bars of approximately 1.5-mm thickness.

Matrix crystallinity

Differential scanning calorimetry (DSC, PerkinElmer Pyris 1 equipped with an Intracooler 2P) was used for the crystallization and melting analysis of the pure PLA and the composites. The samples were placed in sealed 10-mg aluminum pans and scanned under a constant nitrogen purge (20 mL/min). They were heated from −60 to 200°C at a rate of 10°C/min, held at 200°C for 2 min, cooled to −60°C at the same rate, held for 2 min to stabilize, and then further heated to 200°C and held for 2 min before cooling to room temperature. The DSC provided accurate data for the melting temperature (T_m) and the crystallization temperature (T_c). The DSC apparatus was calibrated for temperature using indium and zinc and for enthalpy using indium.

Dynamic mechanical properties

Dynamic mechanical analysis (DMA) was performed in three-point bending mode using a PerkinElmer DMA7e dynamic mechanical analyzer equipped with an Intracooler 2P. A static force of 500 mN and a dynamic force of 415 mN were used with a frequency of 10 Hz over a temperature range of −50 to 120°C at a heating rate of 2°C/min. The samples were cut from the sheets with typical dimensions of 1.3 × 19 × 14 mm. The test specimen dimensions were kept as similar as possible in order to obtain an accurate comparison. The DMA7e was calibrated for force using a standard mass, for temperature using indium, and for distance using a standard metal calibration block.

Scanning electron microscopy (SEM)

The topographies of the composites were analyzed using an SEM microscope (Phillips XL 30 Oxford 6650) with an acceleration voltage of 142 eV. The samples were coated with gold using a vacuum sputter coater.

Optical microscopy

A Nikon Labophot II optical microscope equipped with a Mettler FP90 hot stage was used to analyze the interfacial regions between the untreated and treated natural fibers and the PLA matrix. Specially prepared small sections of composite materials, containing only a minimal amount of fibers, were placed on a glass slide and

TABLE I
Terms to Designate Materials

Designation	Meaning
PLA	Poly(lactic acid)
Unwashed	Flax fibers without pretreatment
Washed	Flax fibers washed in sodium hydroxide solution and extracted with acetone
BA	Butyl acrylate monomer
EHA	2-Ethylhexyl acrylate monomer
C	Mixture of butyl acrylate and methyl methacrylate used
CS	Ethylene dimethacrylate used as crosslinking monomer
NC	No crosslinking monomer added to monomer mixture

inserted into the hot stage. The samples were heated to 200°C and held for 2–3 min and then cooled to 30°C at 5°C/min. The images were captured using a Sony videocamera and video monitor connected to a computer with IPLab image capture and analysis software.

Fungal growth and water aging

Three samples of each system were required for water aging and two samples were used for the fungal growth test. Each of the sample bars were numbered and placed on a ventilated tray in a sealed container containing 2-cm depth water beneath the tray, and they were subsequently placed in an oven at 38°C for 2 weeks. The samples were inspected approximately every 2 days to check for the presence of mold or fungi. This test method is a standard automotive method developed by General Motors (Holden Laboratory test method HN 0028).

For water absorption and mechanical aging, three sample bars from each system were numbered from 1 to 3 to indicate the length of absorption in water (1, 2, and 3 weeks). The samples were weighed prior to being placed into petri dishes containing tap water. In order to keep the samples submerged, a glass slide was placed on top. Each sample was weighed at the same time every day after removing the excess liquid from the surface to ensure consistency in measurements. The samples were removed from submersion after 1, 2, and 3 weeks, according to their number, and were allowed to dry under atmospheric conditions. Each dried sample was subjected to DMA testing under the conditions explained above.

RESULTS AND DISCUSSION

The results obtained for each individual composite are summarized in Table I. We found that the interstitial polyacrylate added about 10% to the total weight of the flax. This was comparable to the amount of water (moisture) normally found in flax. Therefore, it was assumed that the monomer was taking up the voids that were left by the removal of water. Microscopy of the flax showed that the surface was free from polymerization. The initial grafted fibers that were prepared, including the crosslinking monomer, ethylene dimethacrylate, showed evidence of polymer on the surface. Because the polymer was crosslinked, it could not be washed from the surface by acetone extraction. Crosslinking was omitted from further polymerizations so that the polymer would remain soluble and extractable from the surface.

Matrix crystallization and melting

The crystallization temperatures of PLA in different composites are provided in Table II. The composites that contained washed flax fibers had higher crystallization temperatures than composites containing unwashed flax fibers, although in nearly all cases they had a lower T_c than the pure PLA. The removal of waxes and lignin from the flax may enable the flax to better nucleate the crystallization of PLA. A trend that is noticeable from Table II is that all of the composites that contained the crosslinking monomer had a lower PLA melting temperature. The reason for this trend can be explained by the fact that some of the crosslinked polymer resides on the outside of the flax, being unable to be dissolved in acetone, and this could result in the early nucleation of crystals. These crystals were smaller than those in pure PLA, as indicated by a lower melting temperature from the DSC analysis and as observed by optical microscopy (see later).

Dynamic mechanical properties

Graphs of the storage moduli of the unwashed and washed systems used in this work are shown in Fig-

TABLE II
Melting Temperature (T_m) and Crystallization Temperature (T_c) of PLA in PLA–Flax Composites as Measured by DSC

Composite system	T_m (°C)	T_c (°C)
PLA	176.1	105.0
Unwashed A + CS	175.1	102.0
Washed A + CS	175.8	105.3
Unwashed A + NC	175.8	100.8
Washed A + NC	177.5	101.8
Unwashed B + CS	174.3	101.3
Washed B + CS	171.3	102.3
Unwashed C	177.1	101.2
Washed C	177.7	103.9
Unwashed flax	178.3	100.6
Washed flax	176.2	102.5

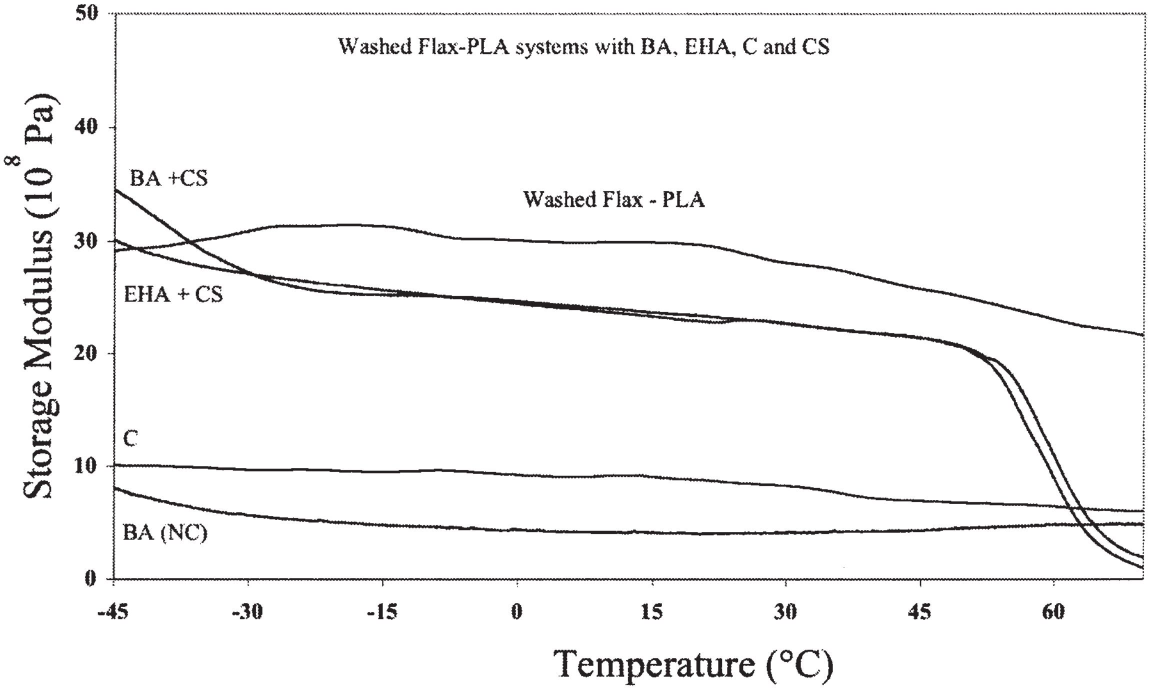


Figure 1 The storage modulus versus the temperature of washed flax composites with butyl acrylate (BA), 2-ethylhexyl acrylate (EHA), copolymer (C), and CS.

ures 1 and 2, respectively. Some of the important results from these graphs are summarized in Table III.

Table III provides the values of the storage modulus and the loss modulus for each composite at ambient temperature. It can be seen that at 25°C the storage moduli of the crosslinked composites were higher than those of other composites without crosslinking agent, excluding grafted unwashed fibers. The storage

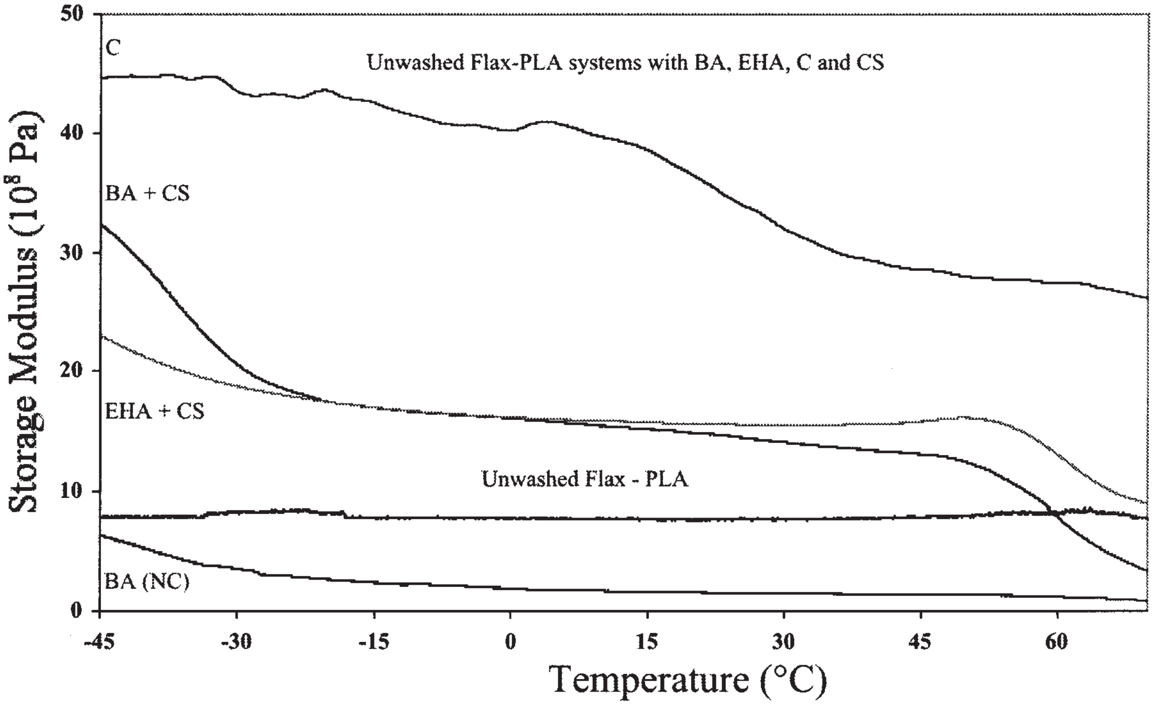


Figure 2 The storage modulus versus the temperature of unwashed flax composites with butyl acrylate (BA), 2-ethylhexyl acrylate (EHA), copolymer (C), and CS.

TABLE III
Thermomechanical Properties of Systems Measured by DMA at 25°C

Composite	Monomer	G' (GPa)	G'' (GPa)	T_g grafts (°C)	T_g PLA (°C)
Unwashed flax	—	0.77	0.08	—	64.9
Washed flax	—	0.40	0.05	—	63.4
Unwashed flax, CS	BA	1.45	0.09	−35.3	58.9
Washed flax, CS	BA	2.31	0.04	−35.3	59.9
Unwashed A	BA	0.15	0.05	−41.1	60.0
Washed A	BA	0.04	0.07	−39.0	61.5
Unwashed B	EHA	1.56	0.06	−50	61.2
Washed B	EHA	2.30	0.10	−50	59.1
Unwashed C	—	3.41	0.35	29.2	73.9
Washed C	—	0.85	0.02	21.7	64.4

G', storage modulus; G'', loss modulus; T_g, glass-transition temperature.

moduli of grafted unwashed fiber composites were much higher than the other composites and much higher than washed fiber composites (see Figs. 1, 2). On further investigation it was noted that the washed crosslinked grafted fiber composites had higher storage moduli than the unwashed ones. This suggests that the adhesion between the flax fibers and the PLA matrix was better with acetone washed flax than with unwashed flax. Therefore, the removal of waxes and lignin associated with unwashed flax results in a better composite material. Figures 1 and 2 show that the storage modulus of unwashed fiber–polyBA and washed fiber–polyBA were the lowest among the tested samples. PolyBA without any crosslinking agent produced a composite that was very soft.

The T_g of these polymers according to Wong et al.[4] is −35°C, whereas the T_g of polyEHA was too low for an exact measurement. However, it is probably about −55 to −65°C. The T_g of the copolymer was found to be approximately −20 to −30°C and that of PLA was observed at about 60°C. Therefore, the composites with polyBA or polyEHA softened at very low temperatures, whereas the choice of the copolymer provided a more suitable higher T_g.

SEM fractography

Figure 3(a–f) shows the surface images obtained from fractographic analysis. The images in Figure 3(a,b) show that there was a difference in the adhesion between PLA and the flax fibers. In Figure 3(a) the surface is cracked throughout the matrix and appears to have an uneven appearance, whereas in Figure 3(b) the surface has a more consistent structure. Even the surfaces morphologies of Figure 3(a,b) were different. The SEM analysis indicated that the matrix–fiber interface was better defined with treated flax. This result indicated why the storage modulus curves for composites of treated flax were higher than the composites of untreated flax. In Figure 3(c,d) a difference was observed between the untreated and treated flax composite surfaces when compared with Figure 3(a,b). In Figure 3(e,f) the composites that contained crosslinking agent have a very smooth surface. These fractographic images indicate that any excess polymer that could not be removed after the polymerization step remained on the fiber surfaces.

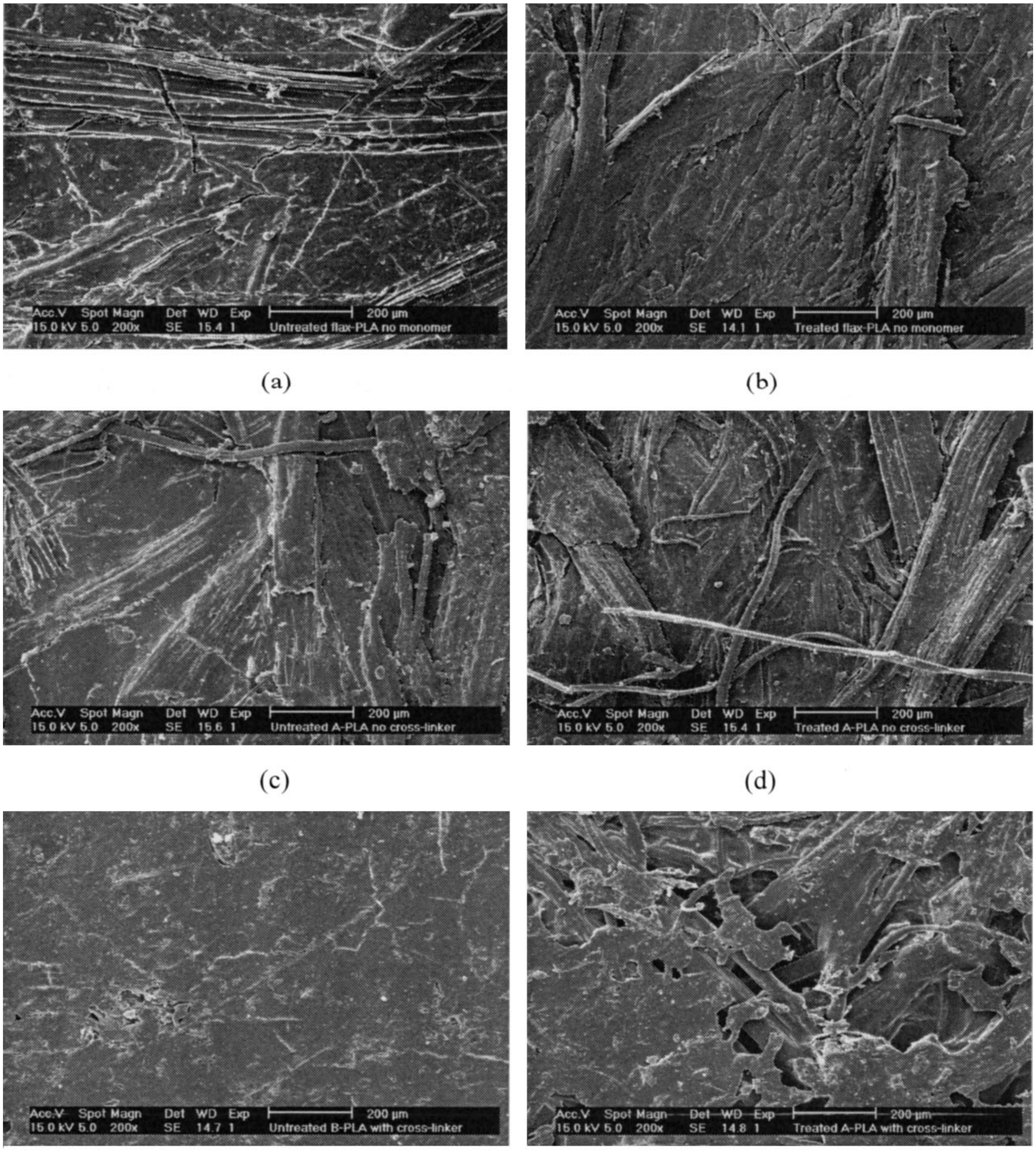
As observed in Figure 4(a–d), there is a difference between the adhesion of the untreated and treated flax fibers to the matrix. In Figure 4(a) there is a continuous fracture between the matrix and fiber, with a buildup of particles along the length of the fiber that is not observed in Figure 4(b). Figure 4(c,d) displays a fracture between the matrix and fiber; however, the treated flax–PLA had a continuous coating of PLA on the flax.

PLA crystal morphology

Optical microscopy was used to observe the formation of crystals during cooling and to analyze the crystalline structure of the composites. From Figure 5(a,b) it is observed that the PLA matrix filled the gaps between the flax fibers and the crystallization process was nucleated from the surface of the flax. Figure 5(c) shows the appearance of excess polymer fragments. Because of this, the crystals started forming around the fragments and results in formation of many smaller crystals as seen in Figure 5(d). It is probable that the lower melting temperature of PLA with crosslinked polyacrylate in the fiber indicates formation of smaller crystals during the cooling cycle.

Water absorption

Figure 6 shows the water absorption of the composites expressed as water gain during the period of immersion. There was a plateau in the absorption



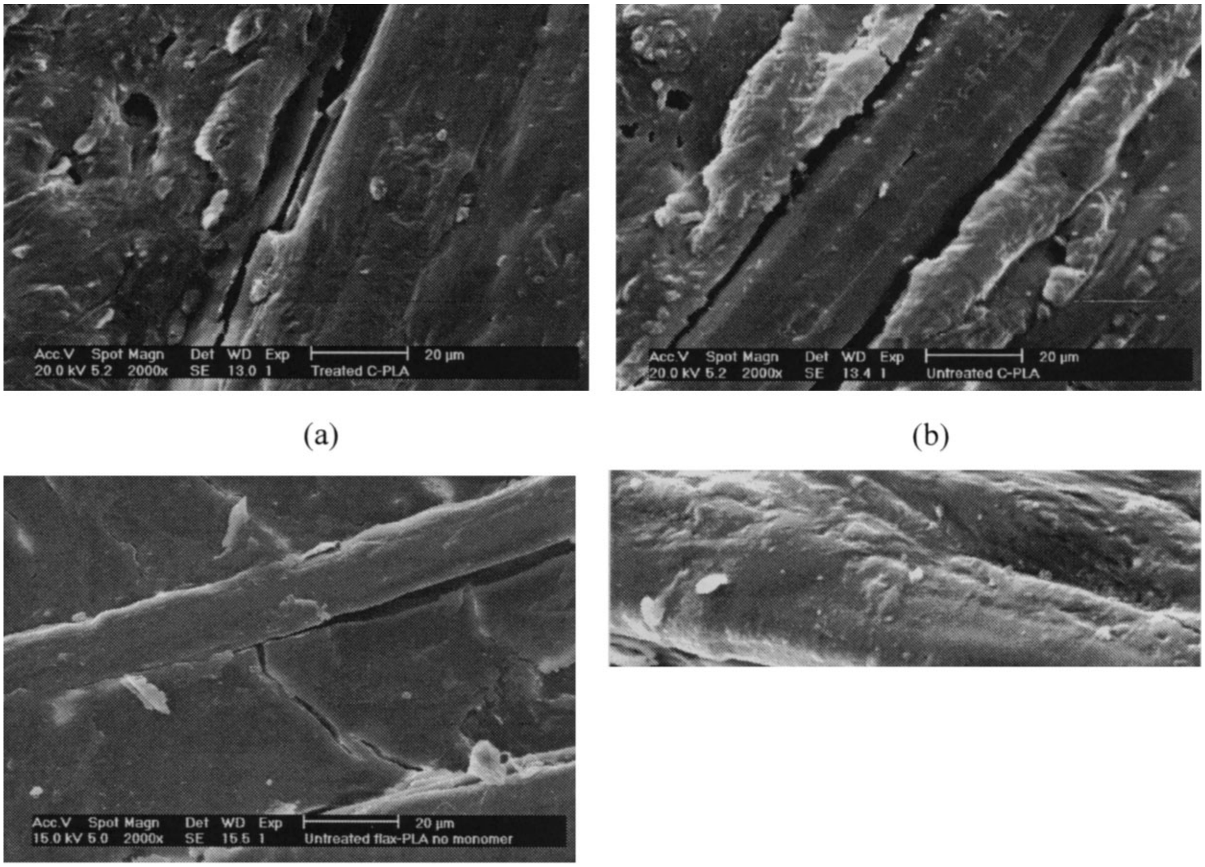
(a) (b)

(c) (d)

(e) (f)

Figure 3 SEM images of (a) unwashed flax (no monomer)–PLA, (b) washed flax (no monomer)–PLA, (c) unwashed flax [butyl acrylate (BA)]–PLA (NC), (d) washed flax (BA)–PLA (NC), (e) unwashed flax (B)–PLA (CS), and (f) washed flax (A)–PLA (CS).

rate after 100 h of water immersion. The rate of water absorption was related to the availability of impurities, such as lignin, and clean cellulose surfaces. Another trend that was noted was that unwashed flax–PLA composites had a higher absorption of water compared with other systems. However, the unwashed grafted flax composites did not follow that trend. This suggested that the absorption of water was mainly attributed to unwashed flax without IP. Polymer grafted flax composites and washed flax composites absorbed less water overall.



(a) (b)

(c) (d)

Figure 4 SEM images of single fiber–matrix interfaces of (a) unwashed flax [copolymer (C)]–PLA, (b) washed flax (C)–PLA, (c) unwashed flax–PLA, and (d) washed flax–PLA.

Fungal growth

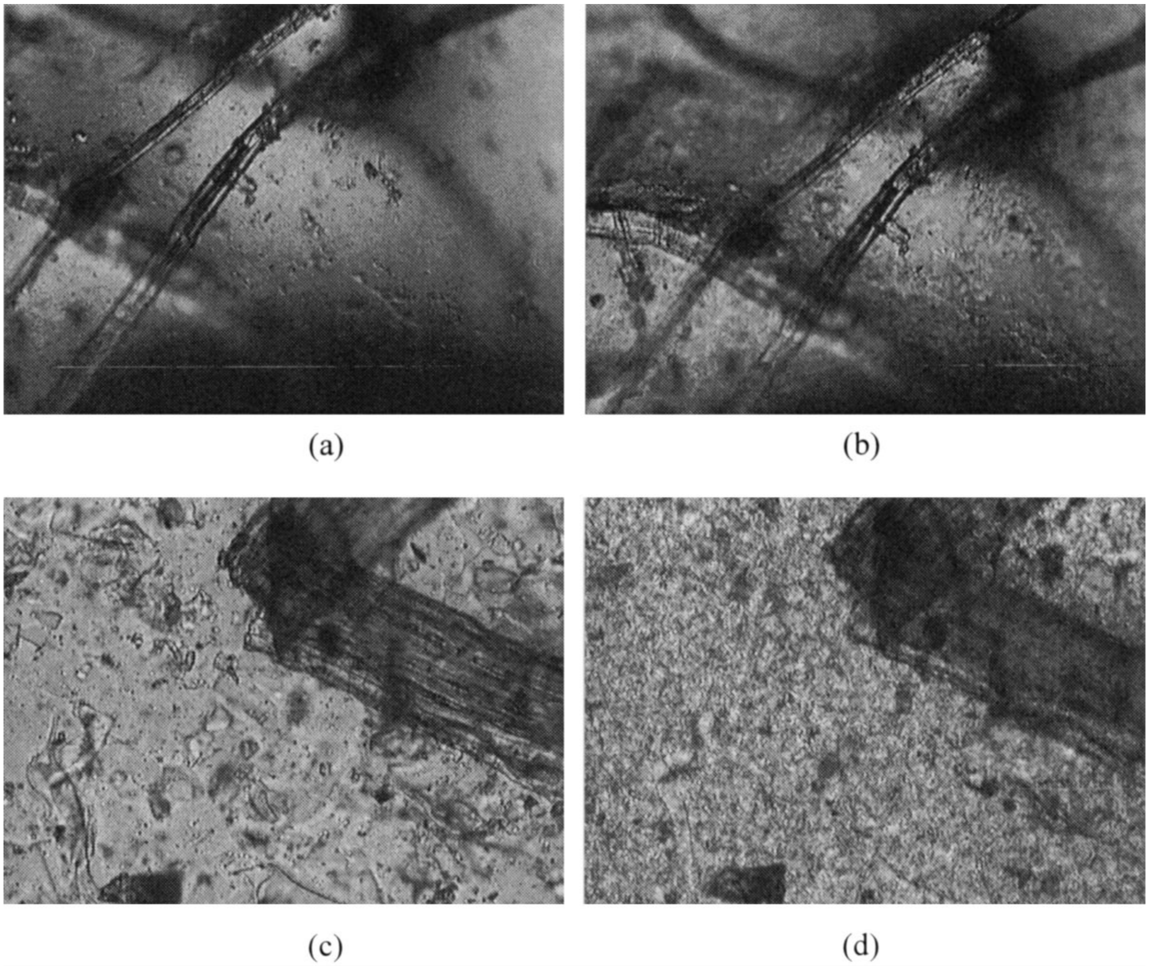
Fungal or mold tests were carried out in accordance with standard specifications in the automotive industry. The results of these tests are provided in Table IV, which demonstrate that impurities in the flax and the ability to absorb water increased the incidence of mold growth. It was clear that the washed flax composites did not exhibit mold. Resistance to mold and fungi increased with lower water absorption. However, the unwashed fiber composites stimulated mold or fungi as denoted by black spores growing from the surface. There was low resistance to mold because of the lignin in the flax. The resistance of the treated flax to mold or fungi growth could be because a nutrient source for the mold to grow was removed by removing the lignin associated with the flax.

TABLE IV
Fungal Growth on PLA-Flax Composites

System	Fungus or Mold	Comments
1. Unwashed flax/PLA	Yes	Black spores formed on surface of composite
2. Washed flax/PLA	No	No apparent sign of molding
3. Unwashed A/PLA	Yes	Black spores formed on surface of composite
4. Washed A/PLA	No	No apparent sign of molding

CONCLUSIONS

The interstitial polymer inside the flax was found to occupy about 10% of the total weight of the flax, which compares with the amount of water removed when drying the flax. The storage modulus of unwashed flax–PLA with copolymer was shown to be much higher than those of the other systems. The washed fiber, crosslinked grafted composites had higher storage moduli than the unwashed crosslinked composites, which suggested better adhesion between the washed flax fibers and the matrix. We found that composites that contained washed flax fibers showed PLA crystallization at higher temperatures than the composites that contained unwashed flax fibers. All of the composites that contained crosslinking agent had a


(a) (b)

(c) (d)

Figure 5 Optical microscopy images of (a) unwashed flax [butyl acrylate (BA)]–PLA (NC, 150°C), (b) unwashed flax (BA)–PLA (NC, 98°C), (c) unwashed flax (BA)–PLA + CS (150°C), and (d) unwashed flax (BA)–PLA + CS (90°C).

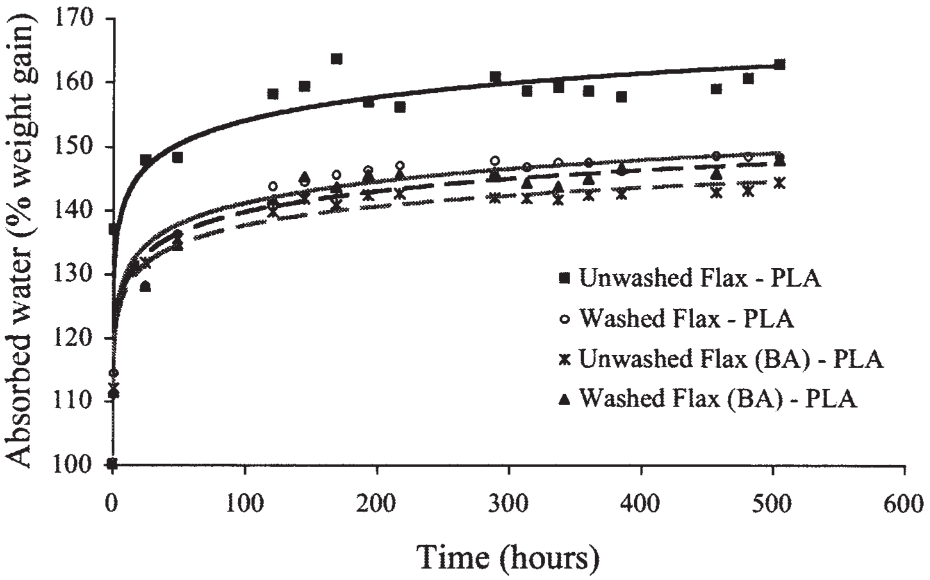


Figure 6 The water absorption for the composites during 3 weeks of immersion in water.

lower PLA melting temperature. This was due to smaller crystals being formed because of the excess polymer fragments on the fiber surfaces of crosslinked grafted composites. In the unwashed flax composites the fracture surfaces were cracked and appeared to have an uneven appearance, whereas in the washed flax composites the fracture surfaces showed a more consistent topography. Unwashed flax–PLA composites had a higher water absorption rate compared with the other composites. Polyacrylate modified flax composites absorbed less water than both washed and unwashed flax composites without polyacrylate. Treated flax composites did not initiate mold growth.

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