

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

R. A. Shanks, A. Hodzic,\* D. Ridderhof

CRC for Polymers, Applied Science, RMIT University, Melbourne, Victoria 3001, Australia

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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, where the flax fibers had been subjected to interstitial polymerization to replace the water in the cellulose fibers. Before 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 as compared with 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 adhesion between flax fibers, and the matrix was improved by the treatments. The composites were subjected to moist environmental conditions to test for development of mold and fungi, and the acetone washed polymerization treated flax composites were resistant to these growths. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2305–2313, 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 behind 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.<sup>1–3</sup> To preserve their environmental and ecological advantages, natural fibers should be used in composites with either biodegradable or recyclable polymers, preferably thermoplastics.<sup>4</sup>

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.<sup>1</sup>

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 wear of tooling, and the possibility of thermal recycling. Possible disadvantages are lower absolute strength and stiffness (in particular impact strength), variable fiber quality, moisture absorption that causes swelling of the fibers, and durability of the composites.<sup>5</sup> These properties need to be improved 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-opening polymerization of lactides, where the lactic acid monomers are obtained from the fermentation of sugar feed stocks.<sup>6</sup> A recent study by Andreopoulos<sup>7</sup> showed that although PLA is inherently brittle, it can be modified by plasticizers,<sup>8,9</sup> which significantly improve 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.<sup>10</sup>

Interstitial polymerization (IP) has been used before with synthetic polymers<sup>11</sup> for improvement of me-

\*Present address: Mechanical Engineering, Sheffield University, Sheffield, UK.

Correspondence to: R. Shanks (robert.shanks@rmit.edu.au).

chanical 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 up to 10% in cellulose fibers. This is designed to eliminate processing difficulties and disadvantages that occur when water and organic materials are combined. This results in (1) conditions for growth of mold and fungi, (2) steaming during molding/melting processes, (3) shrinkage that occurs when water evaporates, and (4) the loss of water during processing that causes friability of natural fibers. All of these properties are expected to be reduced when the water is replaced.<sup>12</sup> 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.<sup>13</sup> 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 can be protected from environmental conditions. IP in natural fibers was used with several acrylate monomers 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 ( $T_g$ ), also known as the softening temperature, of a mixture of two compounds (monomers) can be defined by the Fox equation<sup>14</sup> as follows:

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}} \quad (1)$$

where  $\omega_1$  and  $\omega_2$  are weight fractions of monomers 1 and 2, and  $T_{g1}$  and  $T_{g2}$  are the respective glass transition temperature 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 normally present to be replaced by the acrylate polymer. The modified fibers were expected to provide relatively constant properties under variable humidity, resist mold growth, and be more stable under the elevated temperatures required for compression molding of thermoplastic composites. PLA was chosen as the matrix thermoplastic, since it has a suitable melting temperature; it is derived from renewable materials and 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, al-

though under normal conditions such composites can lose an indeterminate amount of water that will result in lack of control of properties.<sup>15</sup> Polypropylene may require malleation to enhance fiber-matrix bonding with polar cellulosic fibers.

## EXPERIMENTAL

### Materials

Durafiber Flax Grade 1 fiber (95% purity) was supplied by Cargill Inc., Canada. All fibers were dried in a vacuum oven at 60°C for 3 h to remove moisture. Poly(l-lactic acid) (PLA),  $M_n \approx 20,000$  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), and methyl methacrylate (MMA) (BDH Laboratory Supplies), were used for the absorption and polymerization. A crosslinking monomer, ethylene dimethacrylate (Monomer-Polymer Laboratories), was only used during initial polymerizations, since the crosslinking prevented 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. The flax fibers were subjected to Soxhlett extraction with acetone to remove any waxes present. The fibers were then washed in sodium hydroxide (2 mol/L) at 30°C for ~1 h to remove lignin associated with the flax.<sup>6</sup> The sodium hydroxide solution was decanted, and the fibers were washed in water, then distilled water several times, and then 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.<sup>16</sup>

### 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 is expected that some grafting of the monomers onto the flax occurred, but this was not essential to the method. The aim was to absorb a similar amount of monomer to that of the water previously present in the flax, not to maximize the yield of grafting to flax. Initially, ethylene dimethacrylate was used to crosslink the polymer, but polymer that was 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<sub>g</sub> 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) 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 (by vol) 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 tonnes of 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 ~1.5 mm thickness.

### Matrix crystallinity

Differential scanning calorimetry (DSC, Perkin–Elmer 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 and held for 2 min to stabilize, 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<sub>m</sub>) and the crystallization temperature (T<sub>c</sub>). The DSC 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 Perkin–Elmer 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, heating at 2°C/min. The samples were cut from the sheets with dimensions typically 1.3 × 19 × 14 mm. The test specimen dimensions were kept as similar as possible to obtain an accurate comparison. The DMA was calibrated for force using a standard mass, for temperature using indium, and for distance using a standard metal calibration block.

### Scanning electron microscopy

The topographies of the composites were analyzed using a scanning electron microscope (SEM), Phillips XL 30 Oxford 6650 SEM, 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

TABLE I  
Terms Used to Designate the Materials

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

**TABLE II**  
Melting Temperature  $T_m$  and Crystallizing 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

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 inserted into the hot stage. The samples were heated to a temperature of 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 video camera and video monitor connected to a computer with IPLab image capture and analysis software.

#### Fungal growth and water aging

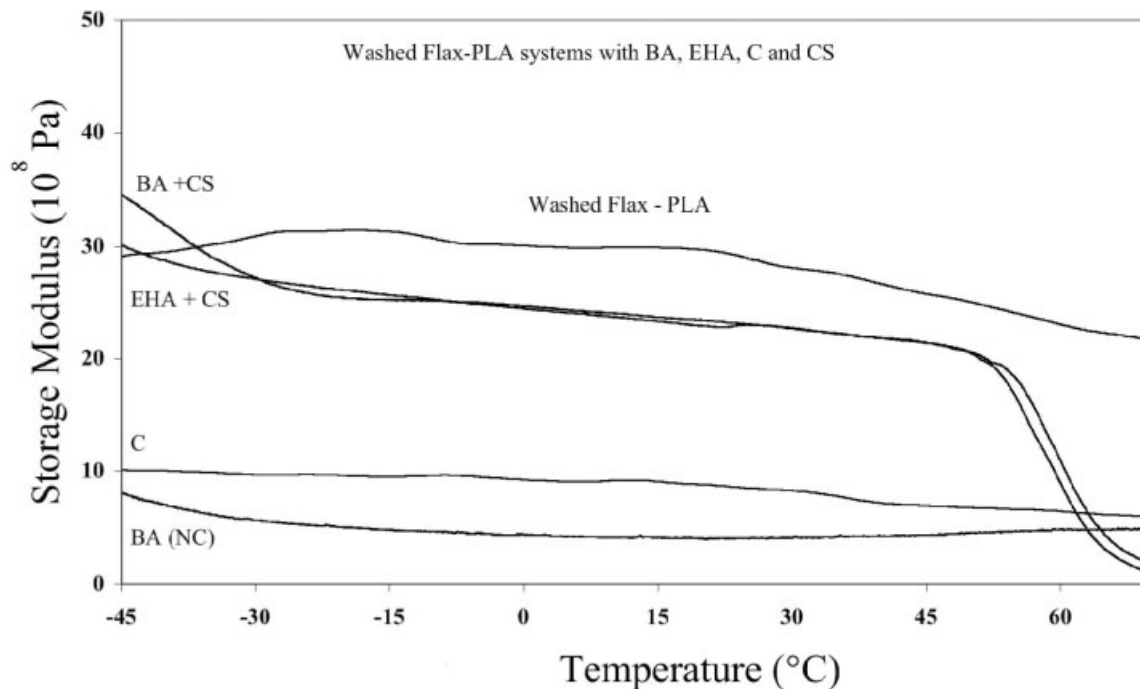
Three samples of each system were required for water ageing and two samples for the fungal growth test. Each of the sample bars were numbered and placed on

a ventilated tray in a sealed container containing 2 cm depth of water beneath the tray, and subsequently placed in an oven at a temperature of 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 before being placed into petri dishes containing tap water. 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 earlier.

## RESULTS AND DISCUSSION

The results obtained for each individual composite were summarized as given in Table I. It was found that the interstitial polyacrylate added about 10% to the total weight of the flax. This was comparable with the amount of water (moisture) normally found in flax. Therefore, it was assumed that the monomer was



**Figure 1** Storage modulus versus temperature of washed flax composites with BA, EHA, C, and CS.

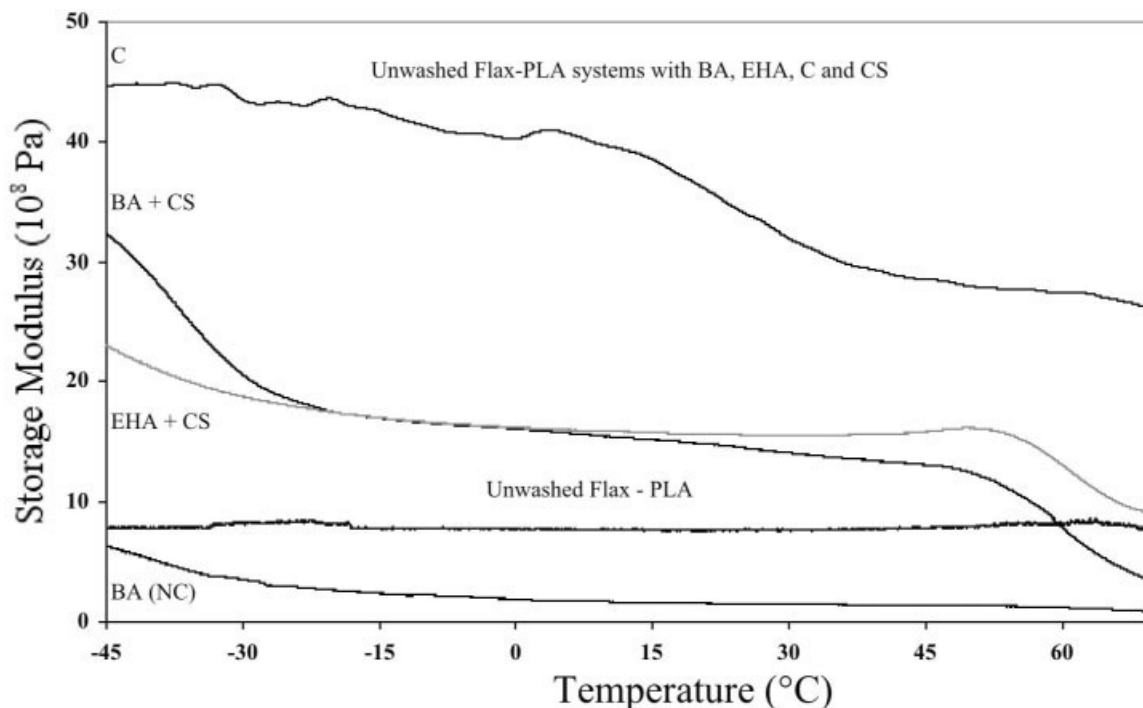


Figure 2 Storage modulus versus temperature of unwashed flax composites with BA, EHA, C, and CS.

taking up the voids that were left by the removal of water. Microscopy of the flax showed that the surface was free from polymerization. Initial grafted fibers prepared including the crosslinking monomer, ethylene dimethacrylate, showed evidence of polymer on the surface. Since the polymer was crosslinked it was unable to 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

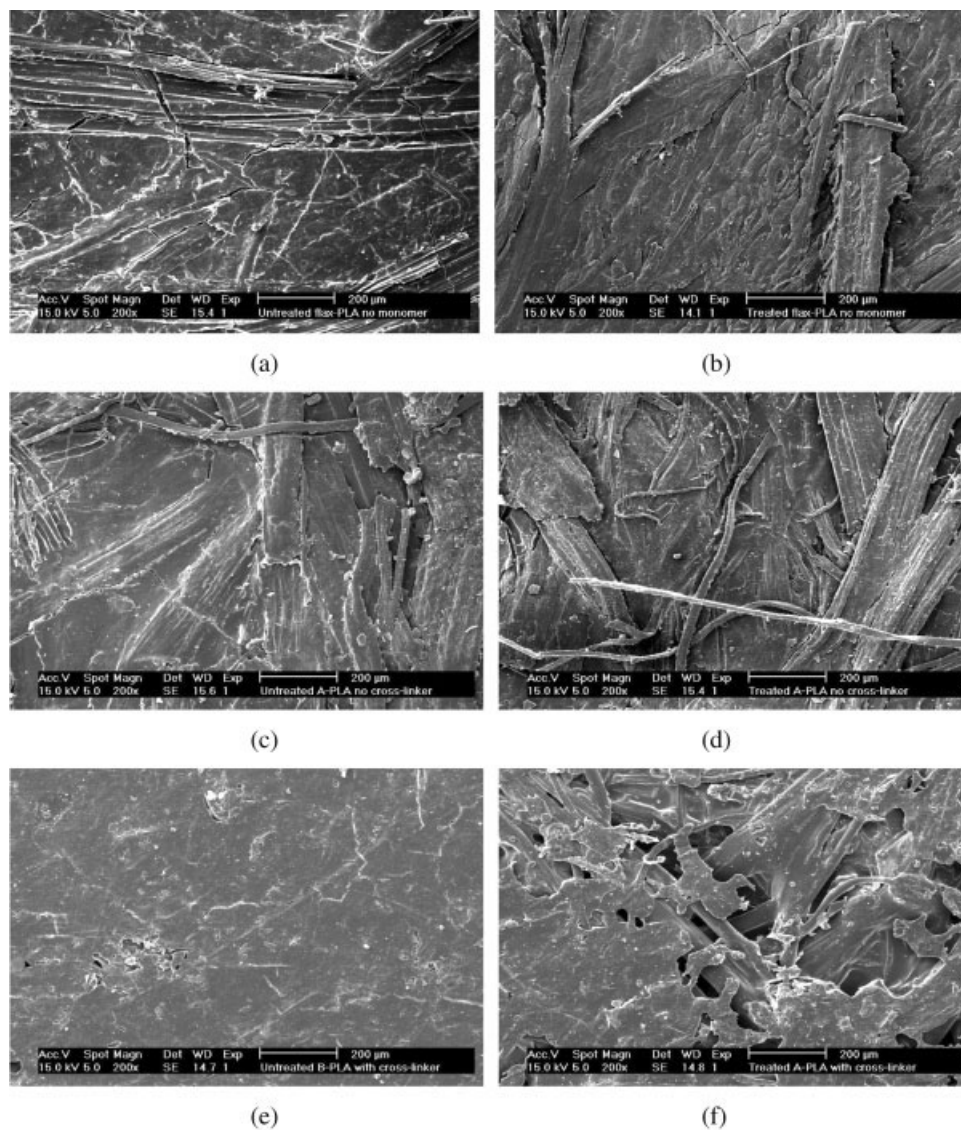
The crystallization temperatures of PLA in different composites are given in Table II. It was found that the

composites that contained washed flax fibers had higher crystallization temperatures than those of composites containing unwashed flax fibers, although nearly all cases had a lower  $T_c$  than that of 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 was 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 tempera-

TABLE III  
Thermomechanical Properties of the 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 at 25°C;  $G''$ , Loss modulus at 25°C, and glass transition temperature  $T_g$ .



**Figure 3** SEM images of (a) unwashed flax (no monomer) –PLA, (b) washed flax (no monomer) –PLA, (c) unwashed flax (BA) –PLA (NC), (d) washed flax (BA) –PLA (NC), (e) Unwashed flax (BA) –PLA (CS), and (f) washed flax (A) –PLA (CS).

ture from DSC analysis and as observed by optical microscopy (see later).

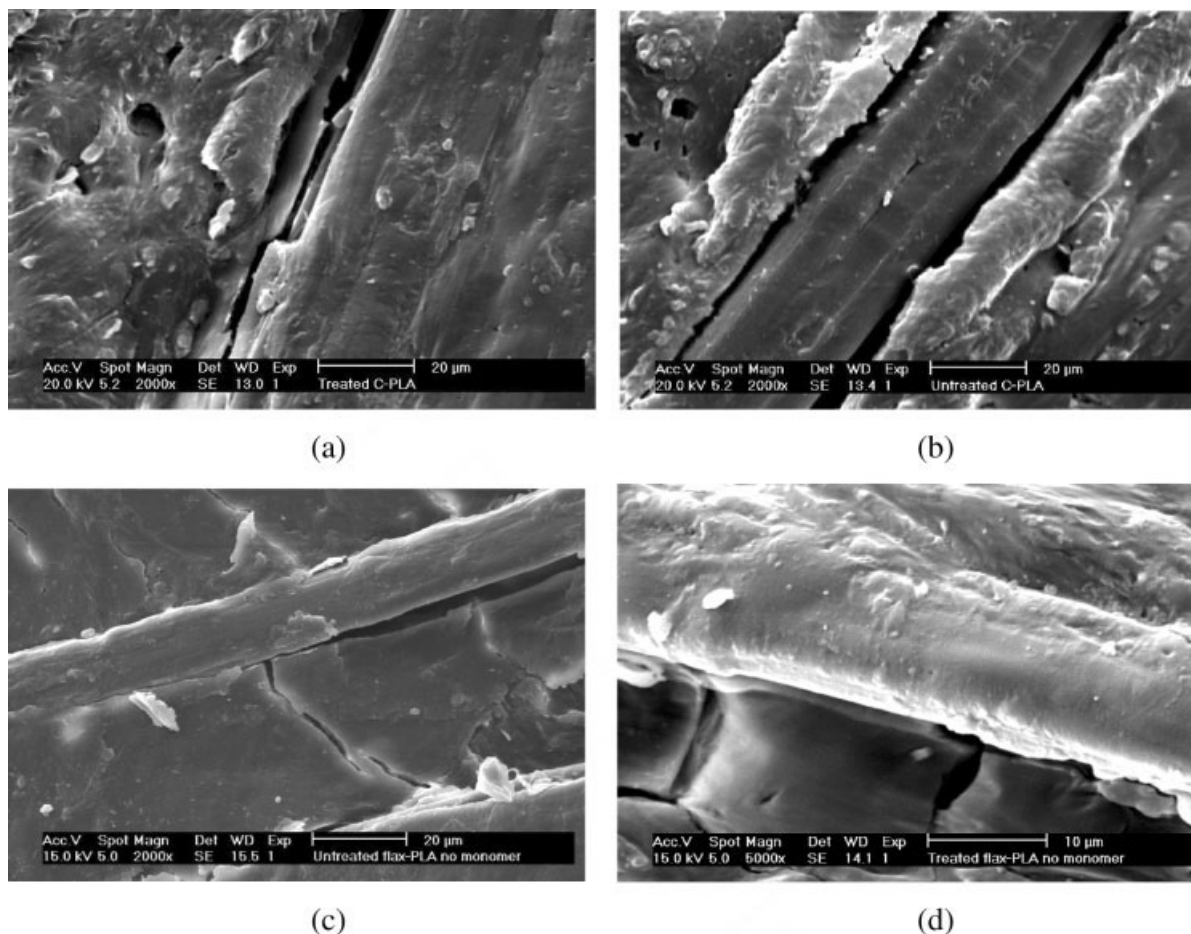
### Dynamic mechanical properties

Graphs of storage moduli of the unwashed and washed systems used in this work are shown in Figures 1 and 2, respectively. A summary of some of the important results from these graphs is given in Table III.

Table III shows 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 modulus of the crosslinked composites were higher than that of other composites, without crosslinking agent, excluding grafted unwashed fibers. The storage modulus of grafted unwashed fiber composites was shown

to be much higher than the other composites, and much higher than washed fiber composites (see Figs. 1 and 2). On further investigation, it was noted that the washed crosslinked grafted fiber composites had higher storage modulus than that of the unwashed ones. This would suggest that the adhesion between the flax fibers and the PLA matrix was better with acetone washed flax rather than the unwashed flax. Therefore, the removal of waxes and lignin associated with unwashed flax results in a better composite material. From Figures 1 and 2, it was shown 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.

T<sub>g</sub> of these polymers was obtained from Li et al.,<sup>4</sup> at a temperature of –35°C, while the T<sub>g</sub> of polyEHA was



**Figure 4** SEM images of single fiber-matrix interfaces of (a) unwashed flax (C) -PLA, (b) washed flax (C) -PLA, (c) unwashed flax -PLA, and (d) washed flax -PLA.

too low for an exact measurement; however, it would seem to be about  $-55$  to  $-65^{\circ}\text{C}$ . The  $T_g$  of the copolymer (C) was found to be approximately  $-20$  to  $-30^{\circ}\text{C}$ .  $T_g$  of PLA was observed to be about  $60^{\circ}\text{C}$ . Therefore, the composites with polyBA or polyEHA softened at very low temperatures, whereas the choice of the copolymer (C) provided a more suitable higher  $T_g$ .

### SEM fractography

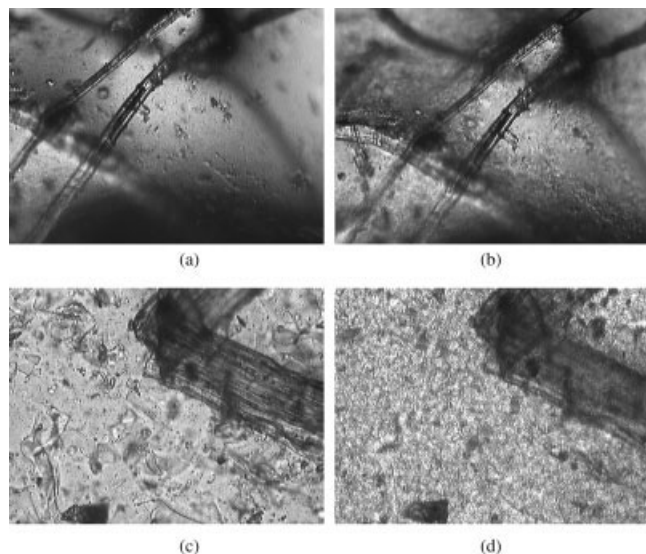
Figures 3(a)–3(f) show the surface images obtained from the fractographic analysis. From the surface images (Figs. 3a and 3b), there was a difference in the adhesion between the PLA and the flax fibers. As shown in Figure 3(a), the surface was cracked throughout the matrix and appeared to have an uneven appearance, whereas in Figure 3(b) the surface had a more consistent structure. Even the surface morphologies of Figures 3(a) and 3(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. Again, in Figures 3(c) and 3(d), a difference was observed between the untreated and treated flax composite surfaces when compared with Figures 3(a) and 3(b). From Figures 3(e) and 3(f), the composites that contained crosslinking agent showed 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 Figures 4(a)–4(d), there is a difference between the adhesion of the untreated and treated flax fibers to the matrix. From Figure 4(a), there is a continuous fracture between the matrix and fiber, with a build up of particles along the length of the fiber that is not observed in Figure 4(b). Figures 4(c) and 4(d) show 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 crystal-

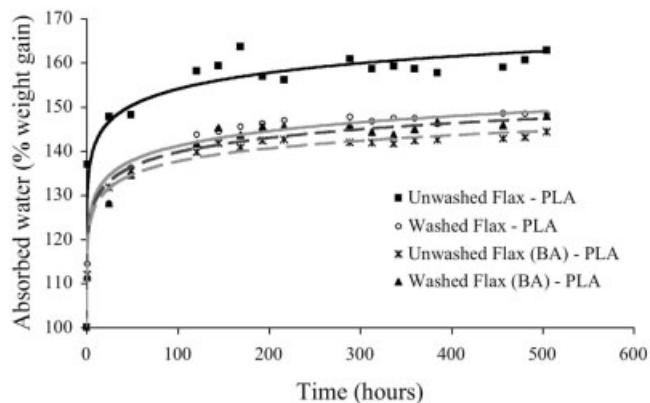


**Figure 5** Optical microscopy images of (a) unwashed flax (BA)-PLA (NC) (150°C), (b) unwashed flax (BA)-PLA (NC) (98°C), (c) unwashed flax (BA)-PLA + CS (150°C), and (d) unwashed flax (BA)-PLA + CS (90°C).

line structure of the composites. From Figures 5(a) and 5(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 resulted 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 immer-



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

**TABLE IV**  
Fungal Growth on PLA-Flax Composites

System	Fungi, mould	Comments
Unwashed Flax/PLA	Yes	Black spores formed on surface of composite
Washed Flax/PLA	No	No apparent sign of moulding
Unwashed A/PLA	Yes	Black spores formed on surface of composite
Washed A/PLA	No	No apparent sign of moulding

sion. There was a plateau in the absorption 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.

### Fungal growth

Fungal or mold tests were carried out in accordance with standard specifications in the automotive industry. The results of these tests are given in Table IV. The results demonstrated 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 lignin in the flax. The resistance of the treated flax to mold or fungal growth could be due to removal of the lignin associated with the flax, a nutrient source for the mold to grow was removed.

### CONCLUSIONS

The interstitial polymer inside the flax was found to occupy about 10% of the total weight of flax, which compares with the amount of water removed on drying of the flax. The storage modulus of unwashed flax-PLA with copolymer was shown to be much higher than that 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. It was found that composites that contained washed flax fibers showed PLA crystallization at higher temperatures than the



composites that contained unwashed flax fibers. In the unwashed flax composites, 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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