

Energy Filtered Low Voltage “In Lens Detector” SEM and XPS of Natural Fiber Surfaces

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ABSTRACT: Most analyses of natural fibers give the average composition of the fiber and not the nature and distribution of surface species present. The nature of the fiber surface is important since it governs interfacial adhesion between fiber and matrix and the transfer of stress to the fiber in composite materials. The surface of caustic treated flax fibers is analyzed using X-ray photoelectron spectroscopy (XPS) and a low voltage scanning electron microscopy (SEM) technique that uses a filtered in-lens electron detector. XPS shows that the fiber surface is not composed of a single polymer but is a mixture of materials, probably degraded lignin and hemicellulose and extractives. The SEM technique shows patches of material on the surface with different contrast and this contrast is shown to result from different average atomic number (Z). The variation in surface composition has obvious implication in variable interfacial properties in composites made using natural fibers. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39572.

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INTRODUCTION

Natural fibers present a sustainable alternative reinforcing phase for composite materials. Composite properties are strongly influenced not only by the inherent modulus of the fiber but also by the interface between the fiber and the matrix. Ligno-cellulose materials have the potential for high modulus due to the inherent modulus of the cellulose crystal, although this is not always obtained in practice because of the complex fiber structure. This article deals with the second issue of a strong consistent interface between the matrix and the natural fiber as this is important in transferring the externally applied stress to the fiber. In particular, this work focuses on techniques to characterize fiber surfaces.

Natural fibers are a complex composite consisting of cellulose, hemicellulose, lignin, pectin and a variety of proteins, waxes, and other organic molecules. These materials are arranged in a complex system, which has multiple purposes in the plant, such as structural support and the transport of nutrients.¹ Compositional ranges for many natural fibers have been reported.² These compositions vary with fiber type, growing conditions and age of the fibers and with the preparation methods for the fiber.^{1–5} Most reports give average compositions of the fibers as a whole but this does not necessarily relate to the materials on the

surface of the fiber. Johansson and Campbell noted that the surface composition often varied substantially from the average fiber composition.⁶ They also proposed that the surface lignin is not evenly distributed but is present in patches on the fiber.

There are few techniques that give information specifically on the surface of a material. X-ray photoelectron spectroscopy (XPS) is a well-established technique that gathers elemental and bonding state data from the upper few nanometres of a surface. It has been used extensively to study wood pulp samples since the pioneering work of Dorris and Gray and to a lesser extent for the study of other natural fibers.^{7–11} Although XPS is useful to give compositional information about the surface, it gives average compositions of the surface and does not give spatial distribution of materials on the surface. Similarly, inverse gas chromatography can also be used to obtain average surface characteristics of fiber surfaces.^{12,13} NIR-FT-Raman has been used to give spatial resolution of the chemical components in natural fibers but this technique requires careful preparation of flat surfaces, does not have high resolution, or the capability to characterize only the surface.¹⁴

The scanning electron microscope (SEM) can provide high resolution topographical information via secondary electron (SE)

images. Conventional SEMs that use high accelerating voltages and conventional “below-lens” detectors or “lower” detectors require conductive coating of the sample to avoid charging artifact and offer very limited material contrast of organic specimens. Using high voltage, the excited volume from which information is obtained can extend hundreds of nanometers below the surface of the sample, depending on the accelerating voltage, and the type of signal and specimen.

In this work, a new generation field emission SEM (FE-SEM) equipped with a modern “in-lens” electron detector was used. These new detectors have various generic names including “upper” detector and “through the lens” (TTL) detector, as well as some more manufacturer specific names. The excellent low voltage resolution of these FE-SEMs allows them to be operated at the E2 charge balance point to enable organic insulators to be imaged uncoated in their unaltered state without charging artefacts.¹⁵ This is achieved because the SE and backscatter electron (BSE) yield are a function of the incident energy of the primary beam. This allows the tuning of the SEM accelerating voltage so that the total electron yield equals the incident beam current and no net charging occurs. The FE-SEM in-lens detector used was the newer “on-axis” type detector with an electrostatic filter grid that allowed for either a pure BSE signal or a mixture of SE and BSE.¹⁶ The in-lens on-axis detector when operated with low accelerating voltages was able to produce unique material contrast of low atomic number materials, with the interaction volume reduced to the tens of nanometer scale.

Historically, the original in-lens detectors were “off-axis” SE detectors that were capable of high resolution images but not material contrast. The material contrast from the modern on-axis detectors used here allowed spatial imaging of different material on the surface, which could be correlated with the XPS compositional information.

EXPERIMENTAL

Materials

The flax yarn was in the form of a fabric, LINEO FLAXPLY, supplied by Lineo n v, Europe. A lignin material, *Indulin AT*, was kindly supplied by the University of Technology Dresden and manufactured by MeadWestvaco. It is a softwood lignin obtained from pine wood. Stearic acid, adipic acid, and ethanol were reagent grade chemicals.

There have been many studies looking at the effect of NaOH treatments on natural fibers.^{17–21} The treatments have ranged from relatively gentle treatments to clean the surface of the fibers and remove contaminants¹⁹ to much more severe treatments that delignify the fiber.²⁰ In this work, the surface condition of the fibers was uncertain so the caustic treatment was undertaken to give a more reproducible surface. The NaOH treatment followed that of Rosa et al.²¹ and was conducted with ~2 g of fibers in a 300 mL beaker with 200 mL of 10 weight/volume caustic, under constant stirring. Treatment was conducted for 2 hr at 60°C. Treatment of the fibers with stearic acid and adipic acid was adapted from the method of Sathasivam and Mas Haris.²² The treatments were conducted with ~2 g of fabric in a 300 mL Erlenmeyer with ~200 mL of

0.2 mol/L of stearic acid dissolved in ethanol at 60°C with constant stirring. A few drops of concentrated H₂SO₄ were added to the flask as catalyst. The treatments with stearic acid were conducted with about 2 g of caustic soda treated fibers, in a 300 mL Erlenmeyer, with ~200 mL of 0.2 mol/L of stearic acid dissolved in ethanol at 60°C, with constant stirring. A water-chilled condenser was plugged onto the Erlenmeyer to prevent evaporation of the solvent. The treated fabric was removed from the flask, washed, and dried.

SEM

The fiber samples were imaged in a JEOL JSM7001 FE-SEM. All specimens were initially imaged uncoated at 1.4 kV accelerating voltage, in both conventional below-lens SE mode, and with the JEOL in-lens on-axis upper electron detector (UED) with a bias filter of –200 volts for BSE mode.

XPS

Data was acquired using a Kratos Axis ULTRA X-ray photoelectron spectrometer incorporating a 165 mm hemispherical electron energy analyzer. The incident radiation was monochromatic Al K α X-rays (1486.6 eV) at 150 W (15 kV, 15 ma). Photoelectron data was collected at take-off angle of theta = 90°. Survey (wide) scans were taken at an analyzer pass energy of 160 eV and multiplex (narrow) high resolution scans at 20 eV. Survey scans were carried out over 12,000 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.05 eV steps and 250 ms dwell time. Base pressure in the analysis chamber was 1.0 × 10^{–9} torr and during sample analysis 1.0 × 10^{–8} torr. Atomic concentrations were calculated using the CasaXPS version 2.3.14 software and a linear baseline with Kratos library relative sensitivity factors (RSFs). Peak fitting of the high-resolution data was also carried out using the CasaXPS software. The sampling size was a minimum of 700 × 300 μm² so atomic concentrations were averaged over many fibers. Variance of atomic concentration measurements were within 10%.

RESULTS AND DISCUSSION

Figure 1 shows SEM micrographs of a flax yarn extracted from a woven flax fabric that has been treated with NaOH for 2 hr at 60°C. The SEI image, Figure 1(a), shows fibers that were partially attacked by the NaOH although the primary fibers had not begun to separate and the fiber bundles were still coated with smooth amorphous material. The surface of the fiber showed some topographical features. There were bands of material perpendicular to the fiber axis, which were nodes in the fiber and there were smaller patches of material on the surface of the fiber.²³ The top right hand corner of the micrograph shows an amorphous mass of material that had the appearance of material that had been dissolved from the surface but which may have been precipitated back onto the surface on the removal of the caustic liquids.

The same region imaged using the upper detector is shown in Figure 1(b). Most of the topological information was lost using this this imaging technique. However, materials with three levels of contrast can be seen on the surface. There were a number of particles giving bright contrast scattered over most of the

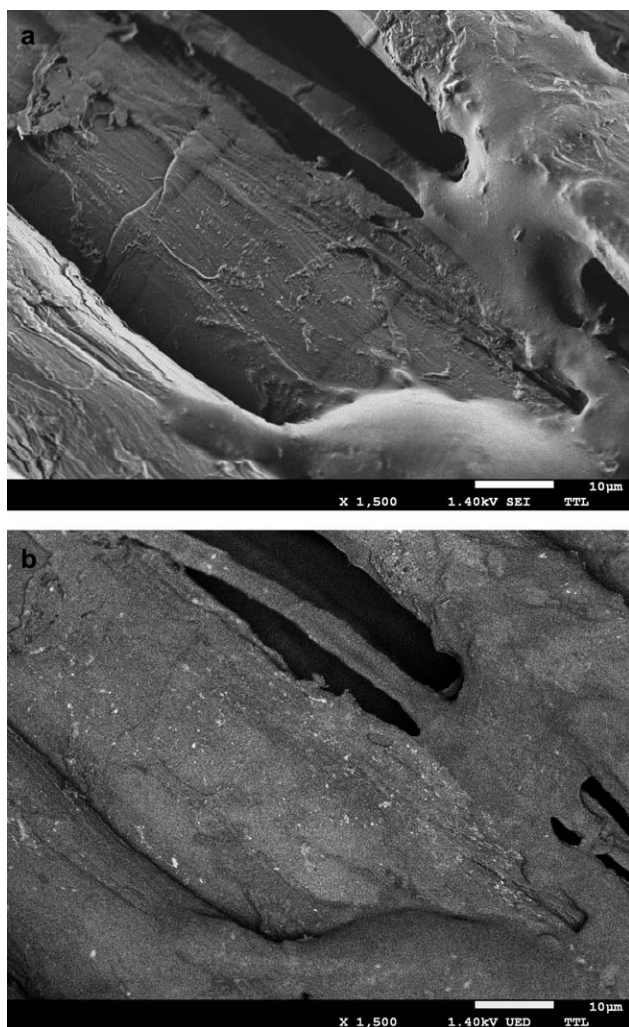


Figure 1. SEM micrographs of NaOH treated Flax fibers: (a) secondary electron image (SEI) using the standard (Everhart–Thornley) below-lens SE detector; (b) same region examined using the upper electron detector (UED) filtered to allow only backscattered electrons.

surface. These were probably inorganic particles or perhaps particles remaining from the caustic treatment. It was not possible to do EDX analysis on these particles in the low voltage through the lens imaging mode. This requires higher SEM accelerating voltages to stimulate the X-rays required and coating of the specimen to control charging. Once the specimen was coated it was no longer possible to get the required low voltage in-lens image contrast. However, several fiber samples were separately examined in conventional SEM mode using EDX that identified particles of three types, namely, silica, particles high in Si, Al, Mg, K, and Fe, and particles high in Ca. It is assumed that similar particles were present in the samples examined in the low voltage though the lens mode shown here.

Of more interest is the blotchy nature of the fibers themselves where material of darker contrast was seen on the fiber surfaces. These regions of darker contrast largely correspond with the patches of material on the surface seen using the SEI mode in Figure 1(a).

These fibers were subjected to XPS analysis in an attempt to elucidate the nature of the surface. Table I shows the composition of the surface of the fibers found in the survey XPS scans. The survey spectra for these fibers showed distinct lines for carbon and oxygen. The lack of nitrogen on the surface eliminated the possibility of proteins on the surface. The lack of inorganic elements suggested that the particles with bright contrast in Figure 1(b) were either some nanometres below the surface so as not to be detected by XPS or were there at concentrations below the detection limit of the XPS.

Natural fibers are a complex composite of cellulose fibers embedded in a matrix of hemicellulose, lignin pectin, and extractives. It is uncertain which of these materials were present on the surface of the fibers as the measured O:C ratio for the fibers did not match any one of these components. This suggested that the surface was complex and probably composed of several different components.

The theoretical O:C ratio for the cellulose repeat unit is 0.83. Values close to this were obtained by Dorris and Gray in pure cellulose samples found in high quality filter papers using XPS survey scans.⁷ Hemicellulose and pectin would both be expected to have a high O/C ratio since both contain glucose rings. The nature of lignin in natural fibers has not been extensively studied but in general, lignin is a complex blend of substituted aromatic materials and would have a much lower O : C ratio to cellulose. Dorris and Gray calculated the O : C ratio for milled wood lignin based on the empirical formula given by Freudenberg and Neish as 0.33.^{7,24} Experimental studies using XPS by Dorris and Gray on samples of spruce lignin gave an O : C ratio of ~0.36, while a commercially available source of lignin studied in this work gave an O : C ratio of 0.20. A caustic soda treatment would be expected to remove some lignin from the surface but it may also leave reaction products on the surface both from the degradation of lignin or from reactions between the polysaccharides and NaOH. Extractives also present an alternative source of low O : C ratio material on the surface. Laine et al. conducted XPS on unbleached kraft wood pulps and found that extractives from the pulp had an O : C of 0.12.²⁵ Zafeiropoulos et al. found low O : C ratios for green flax fiber (0.22) and dew retted flax fibers (0.25).⁸ On the basis of XPS and ToF-SIMS results, they attributed these low values to waxy hydrocarbon like material on the surface. Marques et al. reported that the lipophilic extractives from flax fibers contained a wide range of chemical species such as fatty acids and

Table I. Average Atomic Concentrations of the Surface of Fibres and the Lignin Sample

Material	C (at %)	O (at %)	O : C
Flax yarn NaOH for 2 hr at 60°C	65.9	34.1	0.52
Cellulose (theoretical)	54.5	45.5	0.83
Lignin ⁷			0.36
Lignin (Indulin AT)			0.20
Flax yarn treated with stearic acid ^a	72.9	26.5	0.36

^aRemainder N.

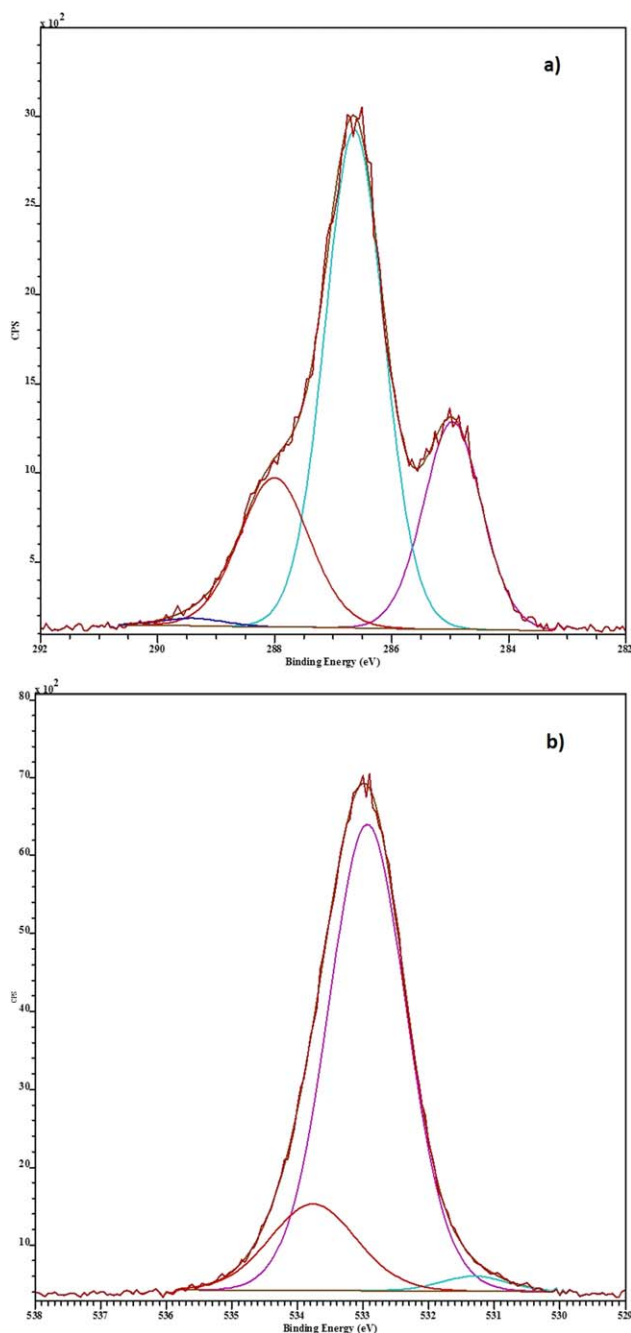


Figure 2. High resolution XPS spectra for the NaOH treated flax fibers: (a) carbon; (b) oxygen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

alcohols, alkanes, sterols, and steroid hydrocarbons as well as aldehydes and ketones.²⁶

Two alternative explanations of the low O : C ratio found here also need to be explored. It is possible that the surface of the fibers was degraded due to X-ray irradiation yielding carbon or hydrocarbons on the surface. However, the exposure times and energies used were within the bounds suggested by Johansson and Campbell to give acceptable levels of degradation.⁶ Johansson and Campbell also suggested that cellulose surfaces are

readily contaminated and that this raises the carbon content on the surface. They suggested that the surface needs to be extracted with acetone to get a clean cellulose surface. High resolution spectra for cellulose (e.g., Beamson and Briggs) also show a small peak at 285 eV, which is usually assigned to hydrocarbon contamination.²⁷ However, the magnitude of the hydrocarbon contamination is usually not large and was not considered sufficient to account for the low O : C ratio found here.

In an attempt to gain more information about the composition of the surface of the fibers, high resolution XPS spectra were also obtained. Figure 2 shows the high resolution XPS spectra for the fibers. The results are tabulated in Table II.

The carbon spectrum was resolved into the four main C bonding states, namely:

- C1 : C bonded singly to C occurring at 285 eV;
- C2 : C bonded singly to O occurring at ~286.5 eV;
- C3 : C doubly bonded to O occurring at ~287.9 eV;
- C4 : C with a double bonded O and a single bonded O, such as in a carboxylic acid or an ester occurring at ~289 eV.

High resolution oxygen spectra were more difficult to resolve. In this work, the oxygen spectra consisted of a central broad peak with shoulders at both high- and low-electron volt. These have been labeled as: O1 at ~531.3 eV; O2 at ~532.9 eV; and O3 at ~533.7 eV.

Each of these bands contained several possible bonds each with slightly different bonding energies and this lead to broadening of the peaks. The possible contributions to the bands listed above following the attribution of Beamson and Briggs²⁷ are:

- O1: C=O (aromatic) at 531.25 eV; C=O* —O (Aromatic) at 531.65 eV
- O2: C—OH (aliphatic) at 532.9 eV; C—O—C at 532.6 eV; C=O (aliphatic) at 532.33 eV; O—C=O* C (aliphatic) at 532.21 eV; C=O O* (aromatic) at 533.14 eV
- O3: O*—C=O C (aliphatic) at 533.59 eV; aromatic OH at 533.64 eV

The actual composition of the surface was difficult to resolve from these spectra. Johansson and Campbell suggested that a raw unbleached flax textile had a surface that was ~66% lignin and 33% extractives.⁶ Zafeiropoulos et al. suggested that flax fibers had waxy like substances on the surface.⁸ There were several features of the quantitative data that suggested the presence of lignin and extractives on the surface. Firstly, the oxygen spectrum had a peak at 531.3 eV. This is characteristic of an aromatic carbonyl or possibly the aromatic acid or ester. Carbonyl substitution on the aromatic group is typically found on ~10% of the aromatic rings in lignin but this may be higher in lignin that has been reacted with NaOH. There was also a very strong C3 peak (12.7 at %) corresponding to carbonyl or ether. Only a small amount of this (0.8 at %) could be attributed to the aromatic carbonyl as it must balance the O1 peak. A key source of this C3 peak could be cellulose. Beamson and Briggs reported that the high resolution XPS carbon scan of cellulose consists of two peaks, C2 corresponding to carbon bonded to a single

Table II. Composition by Bonding State for the Flax Fibres

Sample	C1 (at %)	C2 (at %)	C3 (at %)	C4 (at %)	O1 (at %)	O2 (at %)	O3 (at %)
Flax yarn NaOH 2 hr at 60°C	14.7 (285 eV)	36.0 (286.6 eV)	12.7 (288.0 eV)	0.6 (289.4 eV)	0.8 (531.3 eV)	29.3 (532.9 eV)	6.0 (533.7 eV)
Lignin ^a (Indulin AT)	62.0 (285 eV)	17.0 (286.3 eV)		6.2 (288.9 eV)	5.4 (531.7 eV)	7.2 (533.0 eV)	
Flax yarn treated with stearic acid ^b	35.4 (285 eV)	23.4 (286.5 eV)	9.0 (287.9 eV)	6.0 (289.1 eV)		14.8 (532.5 eV)	9.7 (533.5 eV)

^a Remainder is N.^b Third peak in O spectra at 534.8 eV (1.7 at %).

oxygen (C—OH and C—O—C) and C3 related to carbon bonded to two noncarbonyl oxygens (O—C—O).²⁷ The areas of these peaks were approximately in the ratio of C2 : C3 = 5 : 1, which correlates with the repeat glucose ring for cellulose. In the flax fiber carbon spectrum here, the ratio was ~2.8 : 1. The high resolution carbon XPS of the sample of lignin tested showed a dominant C1 peak and smaller C2 and C4 peaks, Table II. Although lignin can vary between sources, it does contain both methoxy groups and ether linkages between aromatic groups in lignin and these would contribute with hydroxyls to the C2 peak. There was not; however, a significant peak from carbonyl (C3) and this means that lignin would have a high C2 : C3 ratio. Thus, the low C2 : C3 ratio cannot be attributed to lignin. An alternate source of carbonyl could come from the reaction of caustic soda with hemicellulose. This opens the glucose ring giving a chain containing both hydroxyl and carbonyl groups. NaOH/polysaccharide reactions may also generate the small amount of organic acid (C4 = 0.6 at %) found in the flax C spectrum but more likely the C4 peak indicates the presence of a fatty acid on the surface or it may have come from lignin. It is thus postulated that the flax fiber surface consisted of degraded polysaccharide and lignin with a small amount of extractive.

Both the SEM and the XPS clearly indicate that the fiber surfaces were not composed of a single polymer but were a mixture of two or more polymer materials. It was thus postulated that the difference in contrast of regions of the surface seen in Figure 1(b) was a result of different polymer materials on the surface.

BSE imaging is a well-established SEM technique for material contrast at higher accelerating voltages.²⁸ Its usefulness derives from experimental measurements that show a general monotonically increasing backscatter yield with increasing atomic number (*Z*). This forms the basis of atomic number contrast or compositional contrast, where brighter regions of the SEM image have higher average atomic number. It has been reported in the work of Bongeler et al. that a deviation from this relationship was observed at lower accelerating voltages and that in some situations backscatter yield may reduce with increasing atomic number.²⁹ This deviation was further investigated by Assa'd and El Gomati who measured backscatter yield at various low voltages both before and after *in situ* Ar ion cleaning.³⁰ They presented experimental results that showed a clear monotonically increasing backscatter yield with increasing atomic number at low voltages with no deviations. Assa'd and El Gomati explain the results of Bongeler et al. as being due to the very surface nature of low voltage SEM image formation and a thin layer of low atomic number material contaminating the surface of the sample that can be removed by ion cleaning.

These observations suggest that different contrast can be obtained from different organic materials on surfaces due to small difference in average atomic number when very low beam energies are used. To confirm this postulate, a second natural fiber sample was prepared from woven flax cloth onto which a fatty acid, stearic acid, was precipitated. Stearic acid contains fewer oxygen atoms than the flax fibers and should thus have a lower backscattered coefficient and lower contrast to the fibers. The treatment of natural fibers with fatty acids has been used

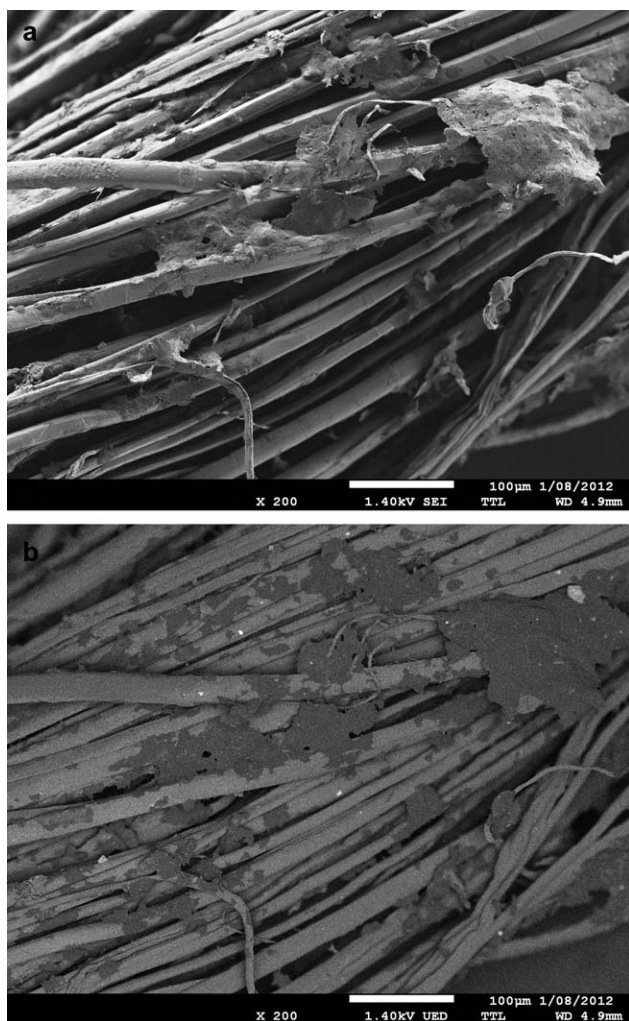


Figure 3. Stearic acid adhering to the flax fibers: (a) secondary electron image (SEI) using the standard (Everhart–Thornley) below-lens SE detector; (b) same region examined using the upper electron detector (UED) filtered to allow only backscattered electrons.

in an attempt to make the surface the fiber more hydrophobic.²² However, here the objective was simply to put a low average atomic number material on the surface to assess the contrast in the low voltage through the lens technique.

Figure 3 shows the SEM image using the low accelerating voltage E2 point charge balance technique. Using the lower detector (SE image), the flax fibers twisted into yarn are clearly seen with the stearic acid appearing as a flake-like material adhering to the surface. Using the upper detector (BSE image), the stearic acid phase had a distinctly darker contrast.

Table I shows that the O : C ratio was reduced on the surface with the stearic acid treatment. The high resolution XPS of the flax fiber treated with stearic acid is included in Table II. As would be expected, the spectra showed a significant increase in the C1 and the C4 peaks. The slight change in the position of the C4 peak to a slightly lower electron volt was consistent with the presence of the ester rather than the acid although the shift may not be significant. The oxygen peaks were also shifted

slightly towards those reported by Beamson and Briggs for an aliphatic ester.²⁷

As a final check on this hypothesis, a treated flax sample was coated with a mixture of stearic and adipic acid since adipic acid contains significantly fewer C atoms than stearic acid and should thus have a higher average Z and appear brighter in the UED SEM image. The result is shown in Figure 4 where again the organic acids were present as large flakes on the surface of the flax fibers. In this case, the flakes displayed distinct regions of different contrast, which was different again to that of the fibers. The oxygen content of the materials was Stearic acid < adipic acid < treated flax fiber, which correlates well with the contrast flax fibers > adipic acid > stearic acid.

Returning finally to the fiber micrographs of Figure 1, the different contrasts can now be interpreted. Higher oxygen content materials have a higher average Z than those with lower oxygen content. Consequently, lignin should appear darker than

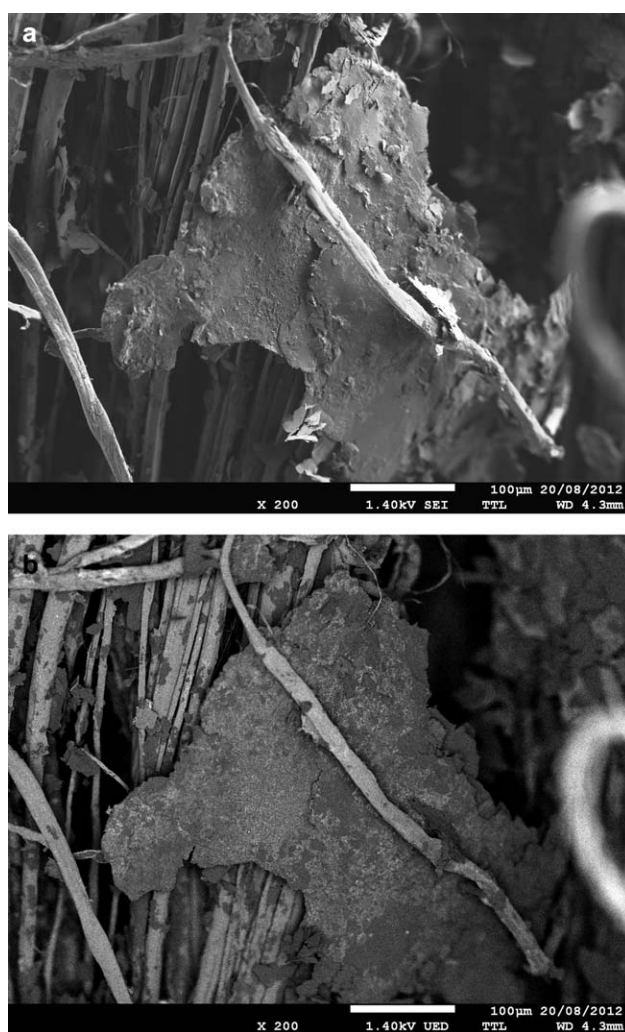


Figure 4. Mixture of stearic acid and adipic acid adhering to the flax fibers: (a) secondary electron image (SEI) using the standard (Everhart–Thornley) below-lens SE detector; (b) same region examined using the upper electron detector (UED) filtered to allow only backscattered electrons.

cellulose/hemicellulose or degraded cellulose. Fatty acids or extractives on the surface would be expected to be darker still since they contain more carbon and less oxygen. Differences in contrast in Figure 1(b) were smaller than that seen in the model system of fatty acid and the base fibers shown in Figure 3. This suggested that the average Z number difference was not high and that if very low oxygen containing materials such as fatty acid extractives were on the surface, they were there associated with materials of higher oxygen containing materials.

The implication of this work in terms of natural fiber reinforced composites is that the surface of natural fibers was not uniform but had materials of different composition in patches on the surface. Consequently, if composites were made using these fibers, the interfacial strength is likely to vary along the fiber lowering their reinforcing efficiency.

CONCLUSIONS

Contrast between different molecular species on the surface of natural fibers was obtained using a low voltage FE-SEM on an uncoated specimen with an in-lens on-axis detector with an electrostatic filter grid that allowed for a pure BSE signal. The contrast was shown to result from small variations in the average atomic number of the different materials. The flax fibers examined here showed surfaces that were not uniform but had regions of different polymeric composition on the surface. This has obvious implications for controlling the interface in natural fiber composites.

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