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Quantitative surface analysis of hemp fibers using XPS, conventional and low voltage in-lens SEM

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ABSTRACT: Surfaces of hemp fibers with different treatments: (1) as received; (2) water washed; and (3) treated with NaOH, were examined using a combination of conventional Scanning Electron Microscopy (SEM), lignin staining and a novel low voltage in-lens detector SEM technique which provides compositional contrast between polymeric materials on the surface. Surface composition determined using quantitative X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS) showed that the surfaces of the as received fibers and the water washed fibers were predominantly lignin and extractives and only after NaOH treatments was there sufficient oxygen on the surface to allow for the presence of polysaccharides. Using the in-lens backscattered SEM technique, spatial distribution of polymeric materials on the surface was shown to be highly non-uniform. The findings have implications for design of natural fiber composites and the interfacial properties between fiber and matrix. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43023.

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INTRODUCTION

The balance between stiffness and toughness of composites requires careful design of the interface between the matrix and the reinforcing phase [see for example Ref. 1]. In natural fiber composites, the interfacial behaviour is problematic because natural fibers are generally more hydrophilic than matrix polymers, hindering wetting of the fibers, and because the surface of natural fibers are physically and chemically non-uniform. This can result in regions of poor interfacial shear strength along the fiber. Knowledge of, and the ability to control, the surface composition is thus important in developing natural fiber composites.

Natural fibers are themselves complex composites consisting of cellulose, hemi-cellulose, lignin, pectin and a variety of proteins, waxes, and other organic molecules. Wang *et al.* reported that raw hemp bast fibers contained 68–78.3% cellulose, 5.5–16.1% hemicellulose, 0.8–2.5% pectin, 2.9–3.3% lignin and some fats and waxes.[2] Others have reported significantly higher amounts of pectin[3,4] and lignin.[3] These variations may reflect different extraction techniques or real variations between samples due to growing conditions, or growth stage of the plant.[5] Fiber composition also changes with chemical treatment. Wang *et al.* showed that cellulose content increased while hemicellulose and lignin decreased during sequential steps of treatment (12 w/w % NaOH, 2 hr), acid hydrolysis (I M HCl, 80°C, 1.5 hr), alkaline treatment (2 w/w % NaOH, 80°C, 2 hr) and bleaching.[6]

Design of the interface in natural fiber composites requires knowledge of the fiber surface. However, most characterisation techniques measure the average composition of the fibers and this may not necessarily correlate to the composition of the surface. Few techniques are surface specific. X-ray photoelectron spectroscopy (XPS) is a well-established technique for characterising surface composition and has been used for the study of wood pulp since the pioneering work of Doris and Gray[7] and, to a lesser extent, for the study of other natural fibers.[8–11] XPS gives the elemental composition of the top ~10 nm of the surface. Its limitation is that it samples a relatively large area (~0.7 mm × 0.3 mm) and does not give spatial distribution of materials on the surface.

Scanning Electron Microscopy (SEM) is traditionally used to give high-resolution topographical information about the fiber surfaces. Conventional SEM techniques produce limited material contrast between organic species and require coating of the samples to avoid build-up of negative charge and associated image distortion. Contrast can sometimes be obtained using selective stains. For example, $KMnO_4$ is known to stain lignin

and has been used to determine lignin distribution in plant cell walls.[12] In previous work, it was shown that an "in-lens on-axis" electron detector when operated with low accelerating voltages at the E2 charge balance point is able to produce backscatter electron (BSE) images with material contrast in low atomic number organic specimens.[13] This allowed spatial imaging of different polymeric materials on fiber surfaces. Moreover, low voltage BSE imaging is a true surface technique with the signal coming from the top 10's nm compared to high voltage SEM which collects data from a much greater depth of several 100's nm.[14]

This article uses a variety of techniques, namely; SEM, $KMnO_4$ staining, low voltage SEM using an "in-lens on-axis" electron detector, and XPS to study changes in surface composition as hemp (*cannabis sativa*) fibers were treated by common methods used in preparing natural fibers for composite manufacture. Information of this type is essential for the control of the fiber/matrix interface which is an important task in composite design.

METHODS

Materials

A non-woven (blown) hemp fiber mat was supplied by the Composites Innovation Centre, Winnipeg, Canada. The hemp variety from which the matt was made was not known but the fibers were most probably mechanically decorticated. It had an average thickness of 6 mm and an average density of 9.1 kg m^{-3}. The exact processes used to prepare the mat were not available. Small ~1 cm square sections of the mat were split open through the thickness and the exposed surface was mounted for XPS and SEM analysis.

Water washed samples were completely submerged in distilled water for 24 hr at room temperature. On removal from the water, the samples were rinsed in distilled water for 1 minute, before air-drying for a minimum of 48 hr. Some of the water washed samples were further immersed in 10% w/v NaOH at 60°C for 2 hr before being thoroughly washed in a stream of distilled water until they had a neutral pH. These samples were left to air-dry for a minimum of 48 hr.

SEM

SEM was performed on a JEOL JSM7001 FE-SEM. Specimens were initially imaged uncoated at 1.4 kV accelerating voltage, in both conventional below-lens Secondary Electron (SE) mode, and with the JEOL in-lens on-axis upper electron detector (UED) with a bias filter of −200 to −300 V for Backscatter Electron (BSE) mode. Selected specimens were later carbon coated and imaged at 15 kV to collect conventional SE images and to perform elemental analysis using Energy Dispersive X-ray Spectroscopy (EDS).

Staining of the fibers by $KMnO_4$ followed the method of Fromm *et al.*[12] Samples of the fibers were stained with 1%(w:w) $KMnO_4$ solution for 1 hr at room temperature. The stained fibers were washed, dried and viewed in the SEM using BSE mode and the in-lens on-axis UED technique.

XPS

Data was acquired using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyser. The incident radiation was monochromatic Al Kα X-rays (1486.6 eV) at 150 W (15 kV, 15 mA). Photoelectron data was collected at a take-off angle of theta = 90°. Survey (wide) scans were taken at an analyser pass energy of 160 eV and multiplex (narrow) high-resolution scans at 20 eV. Survey scans were carried out over 1200–0 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 μ by 300 μ so atomic concentrations were averaged over many fibers. Variance of atomic concentration measurements were ±10% relative.

RESULTS

As Received Fibers

SEM. Figure 1(a) shows a typical fiber from the as-received hemp mat imaged using conventional below-lens Secondary Electron (SE) mode and clearly shows that the fiber surface was not uniform. One end (top left) was relatively featureless but had a somewhat fibrous texture. Higher magnification suggested a coating of smooth amorphous like material. Other parts of the fiber (bottom right) were encrusted with a rough and particulate like substance. This material was most likely remnants of the plant stem structure that had not been removed during decortification. Several fine epidermal hairs can be seen [A in Figure 1(a)] consistent with this interpretation. The standard SE image gave good topographical information but showed little compositional contrast between surface features.

The fibers were also examined with the new technique using the UED filtered to allow only backscattered electrons. The resultant micrograph, Figure 1(b), shows that much of the topographical information was lost using this mode but there were now several levels of material contrast between features on the surface. Particles with bright contrast were seen on the encrusted surface (bottom right) while a small number of similar bright particles were also present on the cleaner sections of the fibers. Of more significance is the variation in contrast between the organic components, in particular the smoother part of the fibers, A, and the matrix of the encrusted region, B.

These fibers were subsequently examined at higher voltage (15 kV) after the sample had been coated to avoid charging. In Secondary Electron Image (SEI) mode using a higher accelerating voltage there was now no difference in the contrast of the matrix phases between the smoother and encrusted regions. The encrusted region displayed many bright contrast particles embedded in the surface of this region, which EDS X-ray analysis revealed were composed variously of Si, Al, Mg, K, O and in some cases Fe and Ca [see Figure 1(a)]. This suggested the presence of mineral silicates while at least one large particle

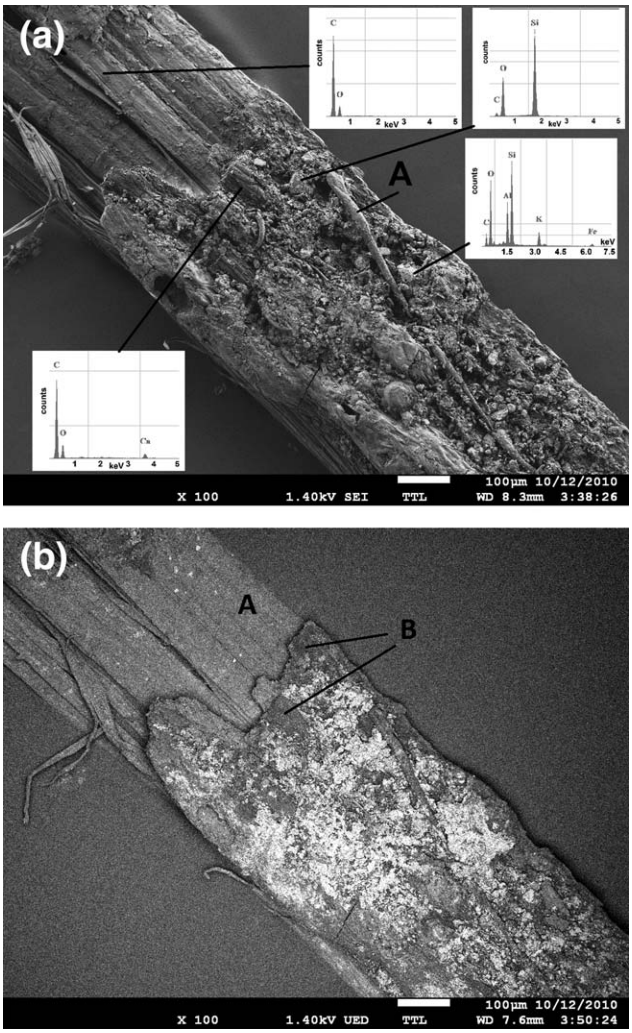

Figure 1. Low voltage SEM micrographs of as received hemp fibers (a) Secondary Electron Image (SEI) using the standard below-lens detector. Inserts show EDS results for selected positions after the sample was coated and imaged at 15 kV; (b) same region using the UED filtered to allow only backscattered electrons.

displayed only Si and O and was clearly silica. Analysis of region A in Figure 1(b) gave only C and O suggesting that this region was purely organic. The polymeric region that had slightly darker contrast in Figure 1(b) was also largely C and O but also contained a small amount of Ca.

Previously, it was shown that using the in-lens UED detector and low voltage, BSE contrast can be obtained between different organic materials based on their average atomic number (Z).[13] Hemp fibers contain mainly polysaccharides (cellulose, hemi-cellulose and pectin), lignin and smaller amounts of extractives. These constituent polymers contain different amounts of oxygen and so have different average values of Z. The theoretical O/C atomic ratio for cellulose is 0.83 and a similar high O/C ratio would be expected for hemi-cellulose and pectin. The O/C ratio for hemp lignin is not available but Dorris and Gray calculated the O/C ratio for wood lignin as 0.33.[7] Measurements in our laboratory of several commercially available lignin samples gave lower values than this of ~0.22. Extractives would also be expected to have a low O/C ratio. Marques *et al.* reported the lipophilic extractives from hemp bast fibers contained a range of chemical species such as fatty acids, alkanes, sterols and steroid hydrocarbons as well as aldehydes and ketones. Linoleic fatty acid, a large component of hemp oil, has an O/C ratio of 0.11.[15] Thus, in terms of increasing brightness using the in-lens UED detector, low voltage BSE:

$$\text{Extractives} < \text{lignin} < \text{cellulose/hemicellulose/pectin} < \text{inorganic particles.}$$

This suggested that the darker contrast encrusted material was higher in extractives and lignin and that the smoother fibrous material might be cellulose. However, staining of samples with $KMnO_4$ showed clearly that the surface of the fibrous material was likely to be lignin. $KMnO_4$ oxidises lignin and reduces the permanganate to MnO_2. The presence of a metal atom should give bright contrast in the Back Scattering mode. Figure 2 shows the as received fibers stained with $KMnO_4$ imaged using low voltage and the UED. The conventional SE image showed similar fiber features to that of Figure 1(a). However, the unencrusted part of the fiber in the UED mode now had a uniform bright contrast indicating that this region had been stained by the $KMnO_4$, suggesting the presence of lignin. The encrusted part of the fiber had a dappled appearance with regions of varying contrast from bright, similar to the smoother part of the fiber, to quite dark. The bright regions indicated some lignin in the encrusted material but there was also a range of non-lignin materials. In particular, a number of globular particles and fibrous regions with dark contrast in the encrusted material suggested material of low atomic number, most likely extractives.

XPS. To quantify the composition of the surface more precisely, the fibers were examined using XPS. Survey scans of the as received fiber gave C and O with a much weaker line for N. There was also a trace of Ca. Other inorganic elements were not detected suggesting the inorganic particles seen in high voltage

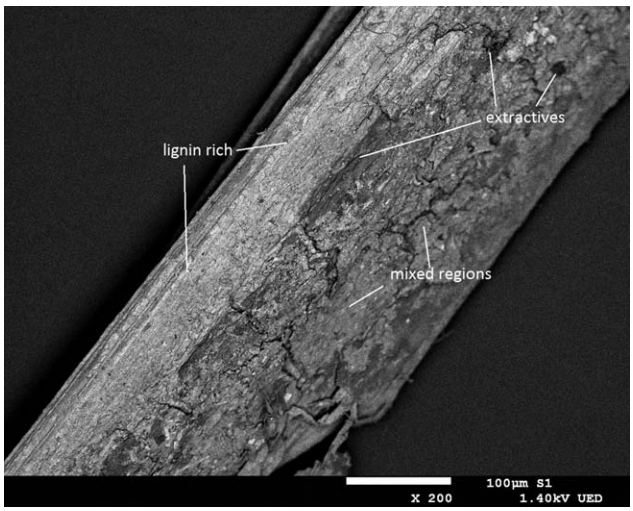

Figure 2. As received fibers stained with $KMnO_4$ and viewed using low voltage and the UED.

Table I. Elemental Analysis of the as Received, Water Washed and NaOH Treated Fibers from the XPS Survey Scans

	Survey scans (at %)				
Sample	C	O	N	other	O/C
As received	72.9	23.3	3.8	Ca	0.32
Water washed	71.9	25.4	2.7	Ca	0.35
NaOH treated	65.5	32.4	1.8	Ca	0.49
Wash water	58.2	29.1	4.9	K(3.5), P(1.2), Ca(2.2), Mg(1.3)	

SEM were likely below the surface of the fiber. Elemental compositions, in atomic %, are listed in Table I.

Figure 3(a,d) are the high-resolution C 1s and O 1s spectra for the as received fibers. High-resolution N scans were also recorded. These scans were quite noisy due to the low concentration of N but showed a broad peak at ~400.3 eV, most probably amide, and a second much smaller peak at 398 eV. It is common to deconvolute the C 1s spectra into 4 essential bonding states, namely: C1 at 285 eV, C bonded to C; C2 at ~286.5 eV, C with a single bond to O; C3 at ~287.9 eV, C with two bonds to O; C4 at ~289 eV, C with three bonds to O. A C5 peak is sometimes seen at ~291 eV related to aromatic groups. The O 1s spectra consisted of a broad central peak at ~533 eV with shoulders at both low ~531.1 eV and high ~534.3 eV binding energies. The O 1s spectra are often ignored as it is difficult to deconvolute the many overlapping peaks. However, they are important for determining surface composition since the O bonding states must balance those of C.

A preliminary fit suggested that there were ~33 at % C—C (C1) bonds on the surface. In addition, nitrogen present as amide would be associated with two carbon atoms and one oxygen, while C4 carbon at ~289 eV indicated acid or ester present on the surface which would also involve oxygen. When the atoms associated with these species and a small O peak at 534.3 eV, which was attributed to absorbed water, were subtracted from the total C and O, then the remaining C/O ratio ~1.95:1. This value demanded that the surface contained few C associated with a single O (e.g., COH, C═O) or C bonded to two O (i.e., O—C—O), restricting the possibility of significant amounts of polysaccharides on the surface. Rather, the non-assigned oxygen on the surface must have been largely C—O—C bonding (i.e., 2 carbons for each oxygen). These were probably associated with lignin, in the form of methoxy substitution on

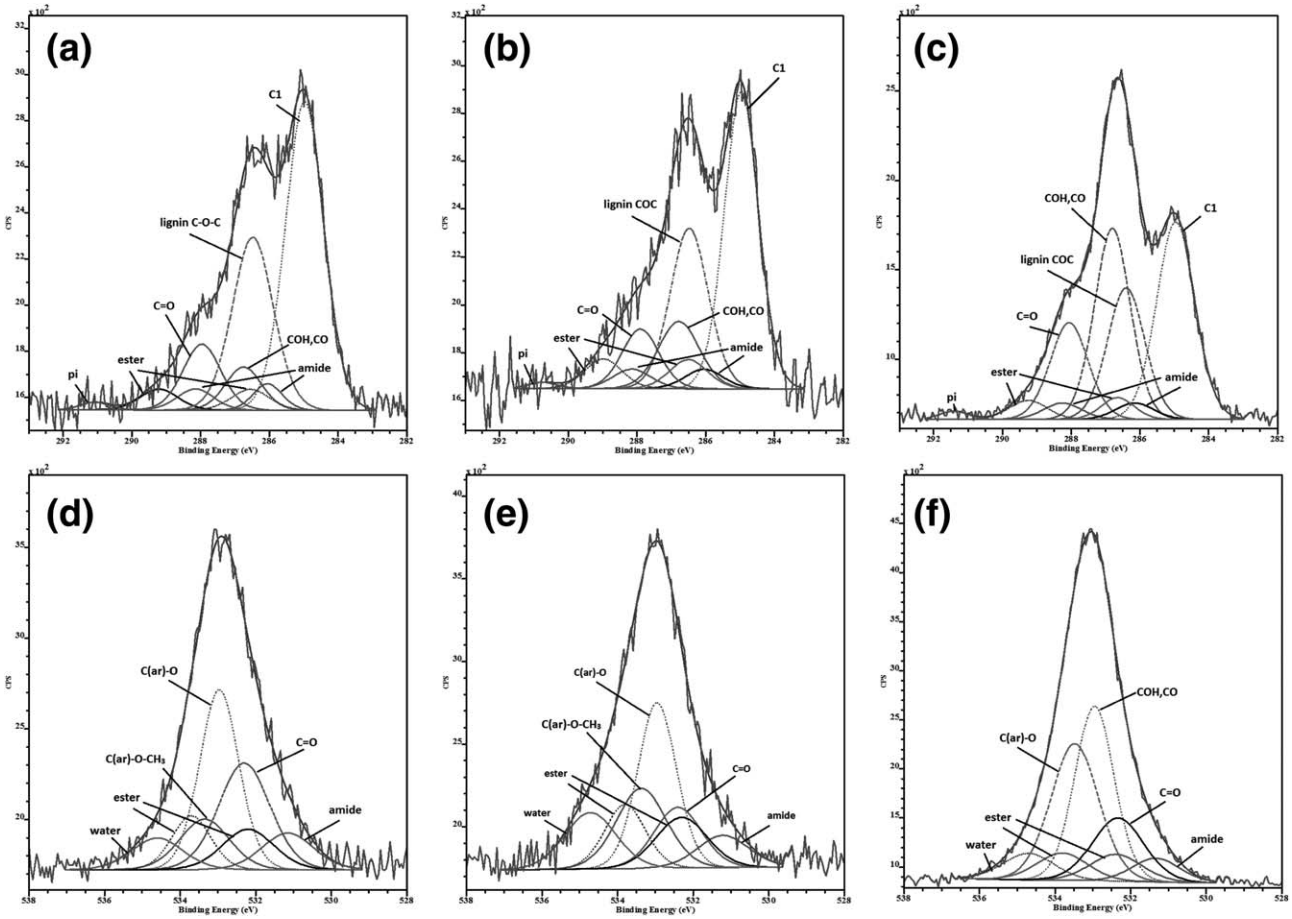

Figure 3. High-resolution XPS carbon spectra for the fibers: (a) C 1s for the as received fibers; (b) C 1s for the water washed fibers; (c) C 1s for the NaOH treated fibers; (d) O 1s for the as received fibers; (e) O 1s for the water washed fibers; (f) O 1s for the NaOH treated fibers as received fibers.

aromatic groups and ether linkages between aromatic groups. It also suggested that the C3 carbon at ~ 288 eV was most likely carbonyl rather than the O—C—O in polysaccharides.

Based on this analysis, the XPS spectra were reconstructed based on the assumption that the surfaces of the as received fibers were predominantly lignin and extractives such as fatty acid/esters. It was also assumed that the nitrogen on the surface was in the form of amides which may have been associated with proteins. Cronin *et al.* noted the possible role of protein in the molecular structure of the cell wall in hemp.[5]

To build-up the spectra the following assumption and procedures were used:

1. The nitrogen was assumed to be there as amide. Amide has a N 1s binding energy at ~400 eV, an O 1s peak at ~531.3 eV and two C1s peaks at ~288.2 eV and ~286.1 eV. The atomic percentages of these peaks must be the same and can be obtained from the at % N at ~400 eV.
2. The acid/ester component, present from fatty acid/ester, was modelled as ester since assuming significant acid present would reduce further the unaccounted for O on the surface. Esters have O1s at ~532.2 eV and ~533.9 eV and C1s at ~289.1 eV and ~286.7 eV. These peaks should have similar at %.
3. The composition of lignin in hemp has not been extensively studied and it is likely to vary with growing conditions and time of harvest. It was assumed to have a large C1 peak due to aromatic groups (~285 eV) and a C2 peak due to methyoxy substitution and aryl ether linkages between aromatic groups. There are numerous other possible substitutions on the aromatic groups but these would be expected to be present at significantly lower concentrations than methoxy.[16] The fit was thus limited to COC and aromatic C. The model for methoxy substitution was taken as poly (4 methoxy styrene) which has C 1s at 286.7 eV(C—OC*H_3), 286.4 eV (C in the aromatic group) and O 1s at 533.4 eV.[17] It was assumed that ether linkages with the C in the aromatic group would also have a binding energy of 286.4 eV. Beamson and Briggs give a range of binding energies (532.98 – 533.45 eV) for an ether oxygen with one or both carbons in a phenyl ring. The best curve fit found here was for a value ~ 533 eV.[17]
4. C–C bonds present in aromatic rings and aliphatic substances such as fatty acid/esters were modelled as a single C 1s peak at 285 eV.

The strong C3 (~288 eV) peak in the preliminary fit could be either C═O or O—C—O. As noted above, the total amount of oxygen on the surface made O—C—O from polysaccharides unlikely. Moreover, it was difficult to fit the O 1s spectra and keep the ester O and C in balance without an O1s peak at ~ 532.3 eV, which corresponds to C═O. Carbonyl substitution on aromatic groups in lignin would give an O1s peak at 531.3 eV. However, the amount of amide present was sufficient to account for the shoulder on the O spectra at this binding energy. It was thus considered that the C3 peak was predominantly aliphatic C═O.

Fitting was achieved by fixing the positions of the various peaks to ± 0.1eV and the peak width half height to 1–1.3 eV for C and 1–1.6 eV for O.

The reconstructed curves are shown in Figure 3(a,d). The components are tabulated in Table II.

Since the residuals for the fitting were very low, the XPS data was consistent with the SEM staining results that indicated a large amount of lignin on the surface of the as received fibers together with some proteins and extractives. There are two aspects to the fitting that need comment. Firstly, the binding energies of the C2 carbon peaks at 286.4 eV and 286.8 eV overlapped and this meant that their peak areas could be varied somewhat within the total envelop for C2 without altering the goodness of fit substantially. The peak at 286.4 eV would have contributions from both the carbons within the aromatic groups bonded to the methoxy oxygen and the two carbons in ether linkages between aromatic groups. The at % of these carbons should be larger than at 286.8 eV that comes only from the methoxy group. However, the relative contributions of the methoxy and ether linkages could not be accurately estimated. Secondly, the large carbonyl peak was not expected. It is possible that it was a product from retting of the fibers but its origin requires further study.

Water Washed Sample

SEM. The suppliers of the fiber mat recommended a simple water wash treatment before use of the mat in composite manufacture. SEM micrographs of the water washed fibers indicated that the fibers were now largely free of the gross encrustation seen on the as received fibers. The fibers, however, were not entirely smooth but had many regions that were still covered with a rough amorphous like material. The UED image of water washed fibers showed similar contrast to the as received fibers with the clean fiber regions displaying light BSE contrast and the regions with the rougher surface texture darker BSE contrast. EDS analysis of the light contrast region at high voltage after coating of the sample showed only C and O while the darker contrast material again showed traces of Ca. $KMnO_4$ staining, Figure 4, showed bright contrast due to lignin staining but this was again non-uniform and patchy. Again there were globular dark contrast particles on the surface and these appeared to be slightly more numerous than for the as received fibers.

XPS. The survey scan data for the washed sampled is tabulated in Table I. The surface contained C, O and N with a minor amount of Ca while there was only a minor increase in O/C ratio over the as received samples. Figure 3(b,e) are the high-resolution C 1s and O 1s spectra respectively. The preliminary fits of the spectra gave a slight decrease in the C1 peak but again when the C—C bonding and oxygen and carbon associated with ester and amide were subtracted, the remaining C/O ratio was approximately 2:1. There was a slight increase in the C4 peak which was consistent with the larger number of dark contrast globular particles and the assignment of these to being fatty ester/acids. Consequently, the data was fitted in a similar manner to the "as received" sample and the components obtained are tabulated in Table II.

Table II. Binding Energies and Concentrations (at %) for the Reconstructed Curves for the High-Resolution XPS of the Fiber Surfaces

Binding energy eV	Chemical bonds	As received at %	Water washed at %	NaOH treated at %	Wash residue Binding energy eV	at %
285	CC	33.1	28.4	19.8	285.0	29.6
286.4/286.5		19.8	17.2	11.2	286.4	18.2
286.8/286.8/286.8		4.4	7.8	19.5	288.1	7.6
288.0/287.9/288.0		7.0	6.2	8.5	289.7	2.7
288.1/288.2/288.2	Amide	2.2	2.1	1.6		
286.1/286.1/286.2	Amide	2.2	2.1	1.6		
286.7/286.5/286.7	Ester	2.2	3.1	2.1		
289.1/289.0/289.0	Ester	2.2	3.1	2.1		
291.0/290.7/291.4	π	0.6	0.5	0.6		
398.1		0.5				
400.3/400.5/400.1	Amide					
	2.1	2.0	1.6			
533.0/533.0/532.9		7.4	7.6	6.0	529.0	0.6
533.3/533.4/533.3		2.6	4.8	4.7	531.4	14.8
532.3/532.4/532.4	C=O	5.7	3.4	4.9	532.7	10.7
533.5				7.5	533.7	3.0
534.6/534.7/534.7	Water?	1.7	3.5	1.7		
531.1/531.2/531.3	amide	2.0	2.0	1.6		
532.2/532.3/532.4	Ester	2.2	3.1	2.1		
533.7/533.8/533.8	Ester	2.2	3.1	2.1		

During washing, a sample of the wash water was collected, the water evaporated off and the waxy residue subjected to XPS. The elemental analysis from the survey scans is given in Table I while data from the high-resolution scans are shown in Table II. The data was fitted to peaks in the broad binding energy ranges. P and K were present in the ratio of 1:2.7 which suggested the presence of K_3PO_4. This assumption was supported by the strong O2 peak at 531.4eV. PO_4^{-3} has an O peak at 531.3 eV.[18] Metal oxides have a binding energy at ~529–530 eV so the Mg and/or Ca was likely there as oxide.

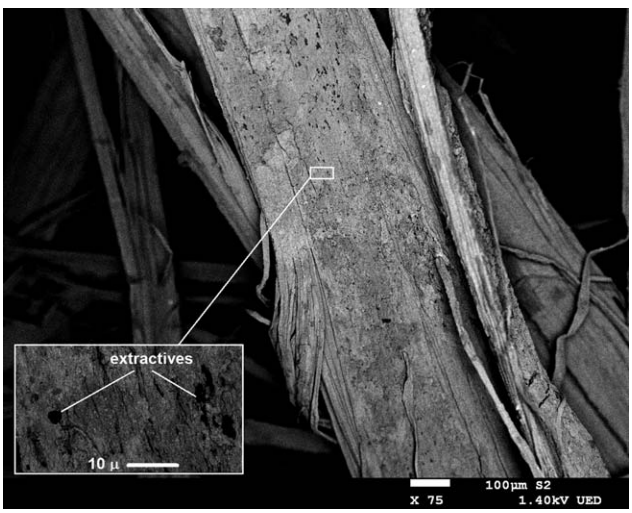

Figure 4. SEM micrographs of water washed hemp fibers after staining viewed using the UED. The insert shows the globular extractives on the surface.

Alternatively, Mg and/or Ca may have been present as carbonate and the presence of $CaCO_3$ was compatible with the spectra. Metal carbonate has a C 1s peak at ~288–290 eV and this should be present in a ratio of 1:1 with the Ca.[19] Here the ratio was Ca:C4 = 2.2:2.7. The O peak from $CaCO_3$ appears at 531.2 eV, which was also a strong observed peak.[19] Alternatively, Ca could have been there as oxalate but this is unlikely as oxalate has an O1s at 533.2 eV and the area of the peak at this position was insufficient as it should have been there at 4 times Ca concentration.[20] A more likely alternative is that Ca might be complexed with pectin.[21] This would not be stoichiometric and so difficult to quantify in XPS.

Thus the surface of the water washed sample was again consistent with the surface being devoid of cellulose but heavily lignin with some extractives.

NaOH Treated Fiber

SEM. Caustic treatments are often applied to natural fibers as a way of reducing lignin and increasing hydroxyl groups on the surface. Figure 5 shows SEM micrographs of hemp fibers treated with NaOH at 60°C for 2 hr. Figure 5(a) is the conventional SE image of a characteristic fiber surface. It shows a roughening of the surface and the beginnings of a break-up of the fiber bundles into individual fibers. The UED image, Figure 5(b), again shows blotchy contrast that could not easily be identified with

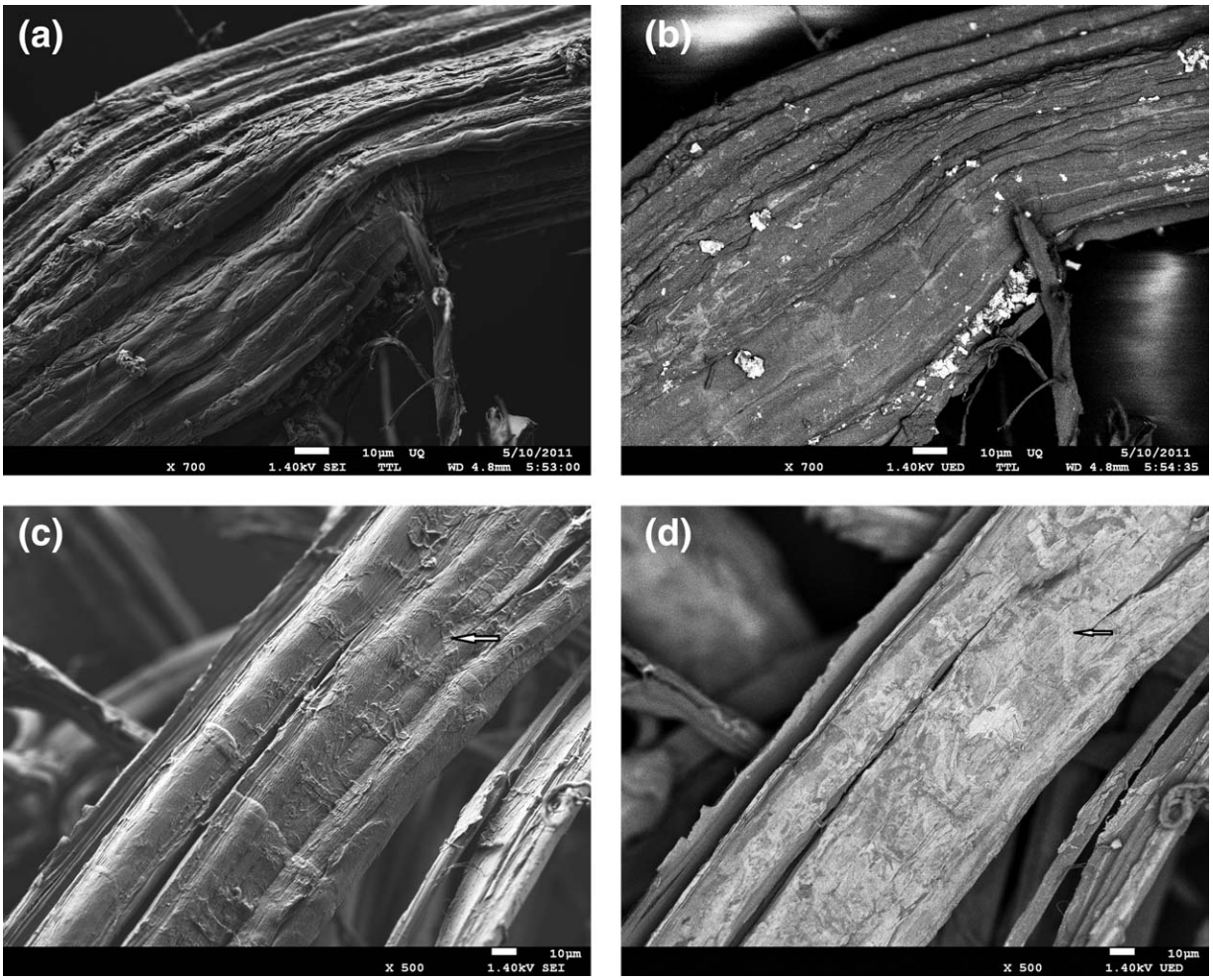

Figure 5. SEM micrographs of the NaOH treated hemp fibers (a) secondary electron image (SEI) using the standard below-lens SE detector; (b) same region using the UED filtered to allow only backscattered electrons; (c) stained and viewed in SEI mode (d) stained and UED image.

topographical features seen in the SE image, Figure 5(a). Particles of bright contrast were again seen on the surface and were again due to a phase containing Ca. The micrographs of the $KMnO_4$ stained samples, Figure 5(d), again showed significant regions of bright contrast consisted with lignin. Of interest is that the ribbon like film material, indicated by the arrows, stained brightly suggesting that these were composed of lignin.

XPS. The survey scans of the surface of the fibers showed an increase in oxygen content with an increase in the O/C ratio to 0.49. This largely resulted from a decrease in the C—C bonding at 285 eV and an increase in the bonding at 286.8 eV (COH/C—O) and to a lesser extent at 288 eV (C with two bonds to O).

In preliminary fits, the ratio of C bonded to O but not associated with ester or amide had now decreased to ~1.5:1. This lower ratio allowed the possibility of some cellulose on the surface as a measurable amount of C with a single bond to O or bonded as O—C—O could now be present. The high-resolution scan for N still contained a peak at ~400.1 eV suggesting amide was again present while the high-resolution C spectra still indicated the presence of an ester or acid component. Consequently, it was assumed that the surface now consisted of a polysaccharide component (cellulose), lignin and extractives.

Beamson and Briggs have presented high-resolution C1s and O1s spectra for high purity cellulose from filter papers with carbon peaks at 286.7 eV and 288.1 eV (ratio ~ 5:1) and oxygen peaks at 532.9 eV and 533.5 eV (ratio 3:2).[17] These peaks overlap those present in the as received and the washed samples so the spectra was fitted with the same peaks as for those samples and the results are tabulated in Table II.

To estimate the actual composition of the surface, it was noted that the total C2 carbon at ~286.4 eV (C—O from lignin with C in the aromatic group) and ~286.8 eV (C—OH and C—O from cellulose and $–OCH_3$ from lignin methoxy) was ~30.7 at % while the total oxygen at ~533 eV (COH and CO from cellulose) and ~533.3–333.5 eV (from lignin methoxy and ether linkages between aromatic groups in lignin) was ~18.2 at %. The lignin oxygen atoms at these binding energies are bonded to 2 carbons while the C2 carbons in cellulose have a single bond to oxygen. Assuming no other contributions to these peaks, an estimate of the oxygen involved in cellulose was

around a third of the oxygen on the surface, which means that there was still <10 at % cellulose on the surface.

DISCUSSION

A key finding from this work was that the surface of the as received fibers and the water washed fibers were significantly different from the bulk composition since they contained little cellulose. Lignin staining and quantitative XPS showed that the surfaces were predominantly lignin and extractives compared to the bulk composition of ~60–80% cellulose reported in the literature.[2–4] Hemp is known to contain slightly higher levels of lignin than other natural fibers such as flax and that the chemical composition tends to be higher in the syringal component than flax.[5] Day *et al.* has shown through $KMnO_4$ lignin staining that flax has lignin in the primary cell wall and at cell corners.[22] It is likely that hemp would have a similar structure. Moreover, studies on the retting of hemp have shown that removal of lignin in hemp is more difficult than in materials such as flax.[22–24] Thus lignin may remain in hemp fibers after retting. The hemp fibers in this work were mechanically decorticated and consequently significant lignin on the surface of the as received fibers and the water washed fibers might be expected.

The contrast between the encrusted cuticle material and the cleaner part of the fibers [Figure 1(b)] was probably due to a higher level of extractives in the cuticle material. Akin has shown that the outer layer in flax fibers is high in extractives which is consistent with the observations for hemp here.[23] The darkest contrast material on the $KMnO_4$ was in two forms, globular material and fibrous material. The spot size in XPS means that average values of the composition of the fibers were obtained and that information on small localised areas was not possible. Although some large globular particles could be identified using conventional SEM imaging through their smooth surface texture, their composition could not be identified with this technique. The combination of $KMnO_4$ staining and low voltage UED imaging, however, clearly indicated that the dark contrast material was low in oxygen but was not lignin. It was thus most likely a fatty acid/ester but the possibility of a protein particularly on the fibrous dark contrast phase cannot be eliminated. Protein would be consistent with the observation of Cronin *et al.* that protein plays a role in the molecular structure of the cell walls of hemp.[5]

Water washing of the fibers was sufficient to remove most of the remaining cuticle material suggesting it was only loosely attached to the surface. It also removed inorganic material and large amounts of nitrogen containing polymers, probably proteins. However, the XPS surface analysis was little changed from the as received sample except for a higher peak in the oxygen spectra at high binding energy which has been attributed to the presence of adsorbed water. The analysis of the wash water suggested that water washing also removed material from within the fiber that was not originally on the surface.

It was only after the caustic treatment that there was sufficient oxygen on the surface to allow for the presence of cellulose. However, the XPS data was consistent with < 10% of the surface being cellulose. The SEM images still showed that there was substantial inhomogeneity in the surface composition. The bright contrast regions of the unstained surface would be higher oxygen containing organic materials while the darker contrast would again be from lignin and extractives.

The variable surface composition has a number of implications for the use of natural fibers in polymer matrix composites. Firstly, lignin is more hydrophobic than cellulose and thus may allow better surface interaction with hydrophobic polymer matrices. It may also result in surface modifications targeted at reacting surface hydroxyls being less successful since there will be fewer available on a lignin surface than one that is predominantly cellulose. Thirdly, the patchy composition of the surface observed here means that interfacial properties of these fibers will vary along the fiber. Areas of weak bonding may act as inherent flaws allowing easy debonding of the fiber/matrix interface under stress. This will tend to reduce the modulus of the composite but may give higher toughness. Thus fiber type and treatment may need to be tailored to the polymer matrix and the balance of stiffness and toughness desired in the composites.

CONCLUSIONS

Hemp fiber surfaces with different treatments were studied using XPS, conventional SEM and a low voltage in-lens detector SEM that provided material contrast between polymeric species. The study indicated that the surfaces of the fibers were non-uniform and remained so even after washing and treatment with NaOH. $KMnO_4$ staining and detailed analysis of high-resolution XPS spectra indicated that the surfaces of the as received hemp fibers and the water washed fibers were predominantly lignin and extractives. The NaOH treated fibers may have had some cellulose on the surface but this was estimated to be less than a third of the oxygen on the surface and therefore < 10 at % of the surface. The in-lens SEM technique showed different polymeric species present in patches on the surface. These findings have clear implications for designing interfaces in composites with natural fibers.

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REFERENCES

1. Hull, D.; Clyne, T. W. An Introduction to Composite Materials, 2nd ed.; Cambridge University Press: Cambridge, **1996**.
2. Wang, H. M.; Postle, R.; Kessler, R. W.; Kessler, W. *Textile Res. J.* **2003**, *73*, 664.

3. Le Troedec, M.; Sedan, D.; Peyratout, C.; Bonnet, J. P.; Smith, A.; Guinebretiere, R.; Gloaguen, V.; Krausz, P. *Compos.: Part A* **2008**, *39*, 514.
4. Garcia-Jaldon, C.; Dupeyre, D.; Vignon, M. R. *Biomass Bioenergy* **1998**, *14*, 251.
5. Cronier, D.; Monties, B.; Chabert, B. *J Agric. Food Chem.* **2005**, *53*, 8279.
6. Wang, B.; Sain, M.; Oksman, K. *Appl. Comp. Mater.* **2007**, *14*, 89.
7. Dorris, G. M.; Gray, D. *Cellulose Chem. Technol.* **1978**, *12*, 9.
8. Zafeiropoulos, N. E.; Vickers, P. E.; Baillie, C. A.; Watts, J. F. *J. Mater. Sci.* **2003**, *38*, 3903.
9. Buchert, J.; Pere, J.; Johansson, L. S.; Campbell, J. M. *Textile Res. J.* **2001**, *71*, 626.
10. Fuentes, C. A.; Tran, L. Q. N.; Dupont-Gillain, C.; Vanderlinden, W.; De Feyter, S.; Van Vuurea, A. W.; Verpoest, I. *Colloid Surf. A: Physicochem. Eng. Aspect* **2011**, *380*, 89.
11. Mitchell, R.; Carr, C. M.; Parfitt, M.; Vickerman, J. C.; Jones, C. *Cellulose* **2005**, 2 629.
12. Fromm, J.; Rockel, B.; Lautner, S.; Windeisen, E.; Wanner, G. *J. Struct. Biol.* **2003**, *143*, 77.
13. Rasch, R.; Stricher, A.; Truss, R. W. *J. Appl. Polym. Sci.* **2014**, *131*, 4379.
14. Goldstein, N.; Echlin, J.; Romig, L.; Fiori, L. Scanning Electron Microscopy and X-ray Microanalysis, 2nd ed.; Plenum Press: **1992**.
15. Marques, G.; Del Río, J. C.; Gutiérrez, A. *Bioresource Technol.* **2010**, *101*, 260.
16. Regauskas, A. Available at: http://www.ipst.gatech.edu/faculty/ragauskas_art/technical _reviews/Basics %20of %20Kraft %20Pulping.pdf. (Accessed 16 Oct. **2013**).
17. Beamson, G.; Briggs, D. High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database; Chichester, England: Wiley: **1992**.
18. Ide-Ektessabi, A.; Yamaguchi, T.; Tanaka, Y. *Nucl. Instr. Methods in Phys. Res.* **2005**, *241*, 685. B
19. Nia, M.; Buddy, D.; Ratnera, B. D. *Surf. Interface Anal.* **2008**, *40*, 1356.
20. NIST X-ray Photoelectron Spectroscopy Database, Available at: http://srdata.nist.gov/xps/Default.aspx. (Accessed 21/11/**2014**).
21. Sedan, D.; Pagnoux, C.; Chotadar, T.; Smith, A.; Lejolly, D.; Gloaguen, V.; Krausz, P. *J. Mater. Sci.* **2007**, *42*, 9336.
22. Day, A.; Ruel, K.; Neutelings, G.; Cronier, D.; David, H.; Hawkins, S.; Chabbert, B. *Planta* **2005**, *222*, 234.
23. Akin, D. E. *ISRN Biotechnol.* **2013**, *2013*, 186534.Article ID
24. Fischer, H.; Müssig, J.; Bluhm, C. *J. Nat. Fiber* **2006**, *33*, 39.