Original article

Textile Research Journal

Textile Research Journal
2015, Vol. 85(19) 2059–2070

DOI: 10.1177/0040517515576322
trj.sagepub.com
SAGE

Dynamic mechanical analysis, surface chemistry and morphology of alkali and enzymatic retted kenaf fibers

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Abstract

Bast fibers grow in the bark layer of many plants and have been used for textiles and cordage for over 6000 years. Bast fibers are expanding into new markets of non-woven fabrics and composite materials, and a comparative assessment of surface reactive groups and mechanical properties after different retting procedures is of value. Here, bast fiber of kenaf (*Hibiscus cannabinus* L., Malvaceae) were prepared by (1) alkali retting with 2% NaOH and (2) enzymatic retting with pectinase, and compared with commercially-available fiber retted by the natural microbe population in ocean water. Fiber structure was analyzed by fluorescence and electron microscopy; fiber chemistry was assessed by Raman and X-ray photoelectron spectroscopy, and by carbohydrate analysis; and mechanical properties were determined by dynamic mechanical analysis. Collectively, these show that enzymatic and microbial retting preserve the natural fiber structure and result in superior mechanical properties compared with alkali retting, which disrupts structure and degrades quality. The impacts of the retting procedure on fiber chemistry, morphology and mechanical properties are discussed.

Keywords

kenaf, retting, mechanical properties, X-ray photoelectron spectroscopy, Fourier transform Raman, natural fiber, cell wall

Kenaf (*Hibiscus cannabinus* L., Malvaceae) is a fast-growing, multipurpose crop with several harvested components: leaves and tender shoots are suitable for forage; seeds have a favorable oil and protein composition similar to cotton seed; the woody core can substitute for a diversity of forest products; and the long bast fibers, traditionally used for cordage, are expanding into modern composite materials.[1–4] Although originating in North Africa, kenaf grows well in temperate regions when there is no danger of frost. In the temperate United States, for example, it regularly yields greater than 20 dry metric tonnes per hectare of total biomass, and it grows well in marginal soils, such as saline soil, without compromising fiber length.[3,5,6] Applications of kenaf include newsprint,[7] textiles,[8] chemical sorbents,[9–11] insulating and noise-absorbing non-woven materials for automobiles and structural applications[12,13] and composite consumer products such as laptop and cell phone cases.[14] Due to its low density and high specific strength, the bast fiber of kenaf can substitute for synthetic fibers such as glass and carbon with the advantages that natural fibers are low cost and biodegradable.[15]

The mechanical properties of plant fibers depend on chemical composition, morphology and internal fiber-pore dimensions, which in turn depend on the process of separating the fibers from the surrounding plant material: a process called retting. In traditional retting, the natural action of microorganisms degrades the relatively soft tissue of the bark faster than the tough bast fibers.[15–18] With field retting, the crop is left in the field during the decomposition period while with water retting, the fresh cut stems are immersed in water

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(e.g., directly in an ocean, river, lake or pond, or in a tank) where microbial communities mediate the retting process. Water retting is faster and produces more uniform and high-quality fiber, but it uses large quantities of water and can contaminate ground water if the retting liquor is not properly treated before being discharged. Both approaches are laborious and are monitored to ensure that the bast fibers separate from non-fibrous material without affecting fiber quality. Notwithstanding, it is often difficult for producers to judge the quality of the retted fiber.

Although traditional retting still occurs, modern industrial retting relies to a greater extent on chemical retting with harsh alkali, or biochemical retting with purified enzyme preparations, principally pectinases.[15–18] Alkali treatment is followed in industry to produce bulk fiber on a large scale. This process is tightly controlled to produce fiber of consistent quality, but natural plant fibers have a porous structure that is often destroyed by alkali treatment.[19,20] Enzymatic retting performs the same function as natural microbial retting either in the field or in water (i.e., the microbes use enzymes to degrade the plant material), but allows greater control since enzyme-to-fiber ratios, temperature, pH and other variables impacting retting are constantly monitored and adjusted. In addition to the retting procedure, plant growth, and in particular fiber age and fiber development within the plant, impacts the mechanical properties of the fiber.[21]

In the work presented here, we analyzed how the duration of alkali and enzymatic retting affects mechanical properties, architecture, surface morphology, chemical structure and biochemical composition of kenaf fibers, relative to a water-retted commercial source, with the aim of correlating the suitability of the retting process with downstream application. We show that enzymatic and microbial retting preserve the natural fiber structure and result in superior mechanical properties compared with alkali retting, which disrupts structure and degrades quality.

Materials and methods

Plant material and retting process

Kenaf (*Hibiscus cannabinus*, cv Tainung II) used in this study was grown in a fertilized and irrigated field in Lane, OK, USA (34°18' N, 96°00' W), during the 2009 season. Stalks were harvested in mid-October after 135 days of growth. The bark layer was stripped from each stalk within 8 hours of harvest and gently oven dried at 80°C for 72 h. The dry weight mass was measured and the bark was returned to the oven for another 24 h. The bark was considered "dry" when the mass no longer changed with additional drying.[22] For consistent experimental material, bark strands from 60 to 100 cm from the base of the stalk were collected in pools of 30 g (dry weight), and adhered at the base (i.e., 60 cm end) using Gorilla Glue (Cincinnati, OH, USA) according to the manufacturer's instructions.

Multifect ME pectinase (Genencor, Rochester, NY) was used for pectinase retting, and the conditions used were based on the manufacturer's product information for optimal pH, temperature and dosage. Bark bundles of 30 g were incubated in 2 L of pectinase solution in polypropylene containers (ThermoFisher, Waltham, MA) at 45°C with orbital agitation at 50 RPM. The pectinase solution consisted of 2.5 mL of Multifect ME pectinase per L (i.e., 0.25% v/v) of formate buffer (6 mL of 90% formic acid per L of water, adjusted to pH 3.85 with NaOH), and was replaced every 24 h. Lower concentrations of pectinase (e.g., <0.1% v/v) had minimal impact on the bark bundles in the desired time frame, indicating also that the acidic conditions had little direct impact on retting. Individual bundles were removed at 48, 96 and 144 h of retting, washed thoroughly with tap water and brushed with a vegetable brush to remove any remaining debris from the fibers. The fibers were then air dried and stored in a climate-controlled room (50% relative humidity, 22°C). Alkali retting was based on prior work with kenaf[18,23] and our own analysis with another fiber crop, *Sesbania herbacea*.[19] For alkali retting, 30 g bark bundles were incubated in 2 L of 2% NaOH (w/v) in polypropylene containers at 45°C with orbital agitation at 50 RPM. Two percent NaOH (w/v) and 45°C are mild treatments relative to the range of treatments previously tested (e.g., 1–7% NaOH at 100°C),[17,23] and were chosen to avoid extreme conditions for reasonable comparison with enzymatic retting. Old NaOH solution was exchanged for fresh solution every 24 h. Individual bundles were removed after 44, 96 and 144 h (this corresponds to 1 day and 20 hours, 4 days and 6 days, respectively), washed, brushed, and air dried as described above. A reference fiber from the International Kenaf Association of kenaf grown and retted during the 2007 growing season was included in our work. This fiber is typical of fiber that can be purchased in bulk quantities, and was chosen as a commercially available standard against which fiber prepared by our methods could be judged. The plants were grown on the Philippine island of Marinduque near the city of Boac (13°26' N, 121°50' E). The plants were harvested, the bark was manually stripped from the plants, and the bark ribbons were bundled together and placed in ocean water for 12 days. After 12 days in the ocean water, fibers were placed in fresh water to clean the ribbons and remove the salt and salt water. Then the fibers were dried and brushed.

Microscopy and spectroscopy

For epifluorescence microscopy, fibers were embedded in 6% agarose and hand sectioned with a razor blade. Images were captured using the natural autofluorescence of lignin polymers in the plant-cell walls and ultraviolet (UV) epifluorescence (340–380 nm excitation, 435–485 nm emission) on a Nikon e600 compound microscope equipped with a DXM1200F camera (Nikon Instruments Inc., Melville, NY) and an X-cite 120 Fluor System (Exfo Life Sciences Division, Mississauga, Canada). ImageJ version 1.45 s was used to measure the cross-sectional area for each string of fiber.[24]

A FEI-Quanta (Hillsboro, Oregon, USA) environmental scanning electron microscope (SEM) was used to get the lateral image of fibers. The analysis was carried out in secondary electron mode at low vacuum using a 15 kV beam current and 3.0 nm spot size.

An Almega XR Raman spectrometer (ThermoFisher) was used to characterize the surface chemistry of fibers and estimate the degree of delignification. An Olympus BX51 microscope (Olympus America, Center Valley, PA, USA) was used to image the fibers in reflectance mode with 10× objective. A 780 nm near-infrared laser was used with spectral resolution of $2\,cm^{-1}$ full width half maximum (FWHM) for ($1\,cm^{-1}$ per charge-coupled device (CCD) pixel element) to get the spectrum with a scanning range from 100 to $4000\,cm^{-1}$.

X-ray photoelectron spectroscopy (XPS) analysis was carried out using monochromatic 1486.6 eV Al Kα radiation with a PHI 5000 VersaProbe (Physical Electronics, Chanhassen, MN, USA) scanning an X-ray microprobe spectrometer. A survey scan with the pass energy of 187.85 eV was carried out to see the elements of interest. Since carbon and oxygen are major elements, the oxygen–carbon ratio was taken as a parameter to quantify the compounds present in the surface of the fiber. The reference binding energy value for adventitious carbon was 284.80 eV, as provided by the instrument vendor. The carbon and oxygen elemental composition were measured using the pass energy of 23.5 eV. The surface charge neutralization was done using a 10 eV Ar^+ ion. The spot size for the X-ray beam was 20 microns with energy of 4.5 W. Shirley background and Gaussian–Lorentzian functions were used for peak fitting. For statistical purposes, XPS and Raman spectroscopy analysis were carried out in three different spots for each sample.

Carbohydrate analysis

The carbohydrate compositions of the retted fiber samples were determined by acid hydrolysis followed by high-performance anion exchange chromatography with pulsed-amperometric detection (HPAEC-PAD). Acid hydrolysis was carried out as per Sluiter et al.[22] In brief, 300 mg of oven-dry material was placed in a 120 mL pressure vessel (Chemglass Life Sciences LLC, Vineland, NJ, USA) and incubated with 3 mL 72% sulfuric acid at 30°C for 60 min with occasional stirring. Deionized water (84 mL) was added and mixed, and the pressure vessels were sealed before incubating for 1 h at 121°C in an autoclave. After cooling to room temperature, an aliquot of each hydrolyzed sample was filtered through a 0.22 μm filter and diluted 100× and 1000× in preparation for sugar quantification by HPAEC-PAD. HPAEC-PAD was conducted on Dionex (Sunnyvale, CA, USA) ICS 2500 equipment with CarboPac PA20 guard and analytical columns and 2 mM NaOH eluent at $0.5\,mL\,min^{-1}$ and 30°C. Sample injections were either 10 or 25 μL and were run for 20 min using the carbohydrate PAD waveform preprogrammed by Dionex. The column was washed with 200 mM NaOH for 10 min and equilibrated with 2 mM NaOH for 10 min between samples. The neutral monosaccharides arabinose, galactose, glucose, mannose and xylose were quantified against standard curves established with purchased sugars (Sigma-Aldrich, St. Louis, MO, USA).

Dynamic mechanical analysis

The viscoelastic properties of individual fibers were measured using a Rheometric Solids Analyzer 3 dynamical mechanical analyzer (RSA III TA Instruments, New Jersey, USA), operating in the tension mode. The tensile fixtures were used for clamping the fiber strands. The storage modulus (E') was measured relative to temperature: samples were scanned at a heating rate of $2°C\,min^{-1}$, at a frequency of 6.25 Hz and a strain amplitude of 0.2% (determined to be within the linear region of the stress–strain curve) from a separate strain amplitude sweep at 1 Hz) between 25°C and 35°C. A 5 mm sample length was used for all fibers. The cross-sectional area of each fiber was determined by epifluorescence microscopy for input into the dynamical mechanical analysis measurements. Ten fibers were chosen for each variable to calculate the average values and standard error of the mean. Outlier data points differing from the median by more than 1.5× the interquartile range were excluded.

Results and discussion

Cross-sectional architecture of retted fibers

Bast fibers were retted from 135 day-old kenaf stalks by treatment with alkali or a purified pectinase preparation for various times, or were obtained from a water-retted commercial source, as described in Materials and

methods. The impact on fiber structure was first analyzed by epifluorescence optical microscopy, taking advantage of the natural auto-fluorescence of lignin in the cell walls (Figure 1). We previously established that the individual fiber cells within the bast fibers have widths ranging from 10 to 20 μm[21] and this is consistent with the bast fibers used in this study (Figure 1). Alkali retting, even with the shortest treatment of 44 h (Figure 1a), caused consistent swelling of the ligno-cellulosic cell walls of the fiber to occlude the internal pore of each fiber cell and reduced the clarity of the porous honeycomb architecture of the fiber strand. Longer retting times of 96 and 144 h in alkali enhanced this effect (Figure 1c, e). Enzymatic retting with pectinase (Figure 1b, d, f) and water retting with a natural microbial population (Figure 1g) however retained the honeycomb architecture and pore-dimensions of unretted fibers (Figure 1h, unretted fibers as they appear in fresh kenaf bark). The difficulty of sectioning the tough bast fibers created regions in each field of view that were out of focus (Figure 1), but focusing up and down on the sections revealed that alkali retting resulted in uniform occlusion of the pore, while enzymatic and microbial retting left the pore and cell-wall structure uniformly intact.

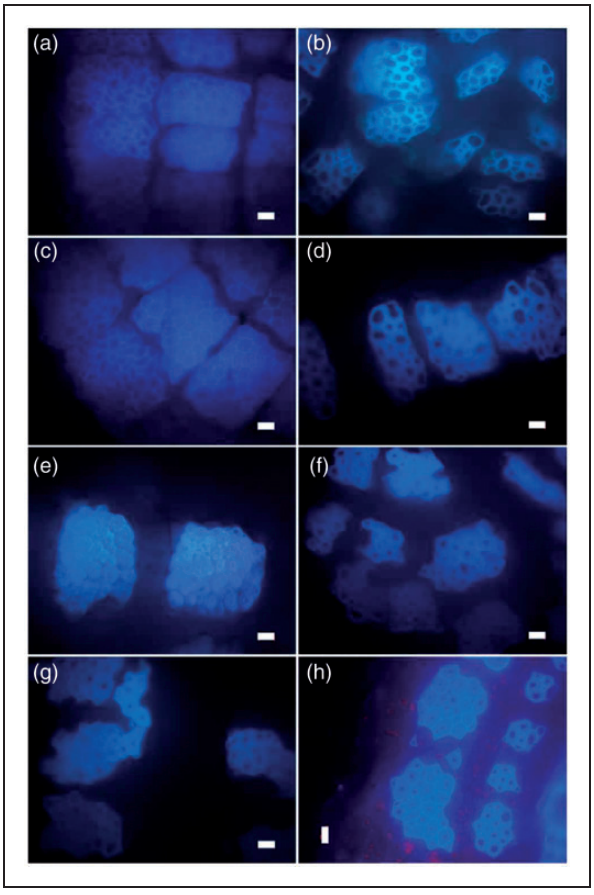

Figure 1. Ultraviolet epifluorescence cross-sectional images of retted kenaf fibers and fibers in unretted bark strips. Retting treatment and duration were with 2% NaOH (w/v) ((a), (c), (e)) for 44 h (a), 96 h (c) and 144 h (e); and with 0.25% pectinase solution (v/v) ((b), (d), (f)) for 48 h (v), 96 h (d) and 144 h (f). For comparison are shown fibers from a commercial source retted in ocean water (g) and unretted fibers in intact, fresh bark strips (h). The intense blue fluorescence signifies lignin content, red fluorescence ((h) only) is from chlorophyll in the fresh tissue; the scale bars in all images are 20 μm. (Color online only.)

Surface morphology

Scanning electron microscopy was used to evaluate the fiber surface structure after retting, since this will contribute to fiber behavior in subsequent applications, including the interaction between the fiber and polymer matrix in composite materials. After 44 h of alkali retting, fiber bundles were poorly separated

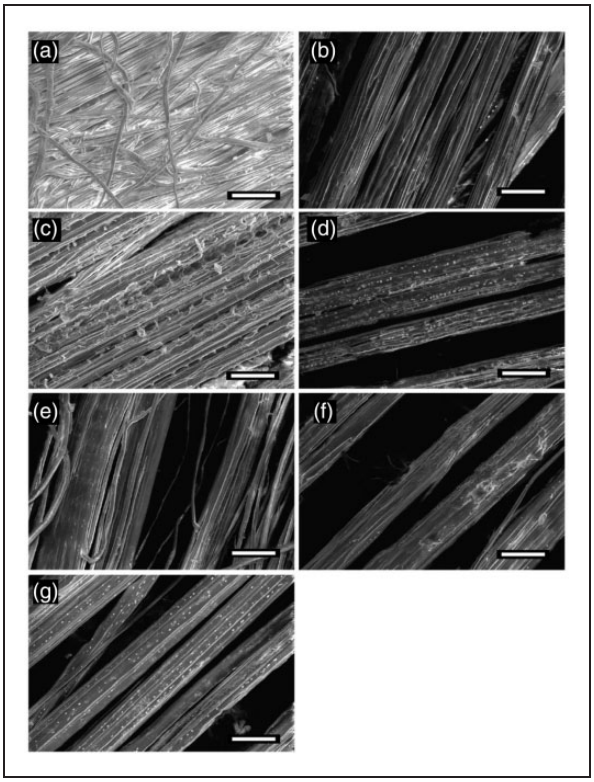

Figure 2. Surface morphology of kenaf fibers by scanning electron microscopy. Retting treatment and duration were with 2% NaOH (w/v) ((a), (c), (e)) for 44 h (a), 96 h (c) and 144 h (e); and with 0.25% pectinase solution (v/v) ((b), (d), (f)) for 48 h (b), 96 h (d) and 144 h (f). For comparison, fibers from a commercial source retted in ocean water are shown (g). The scale bars in all images are 100 μm; note that the width of fiber bundles and individual fiber cells are consistent with Figure 1.

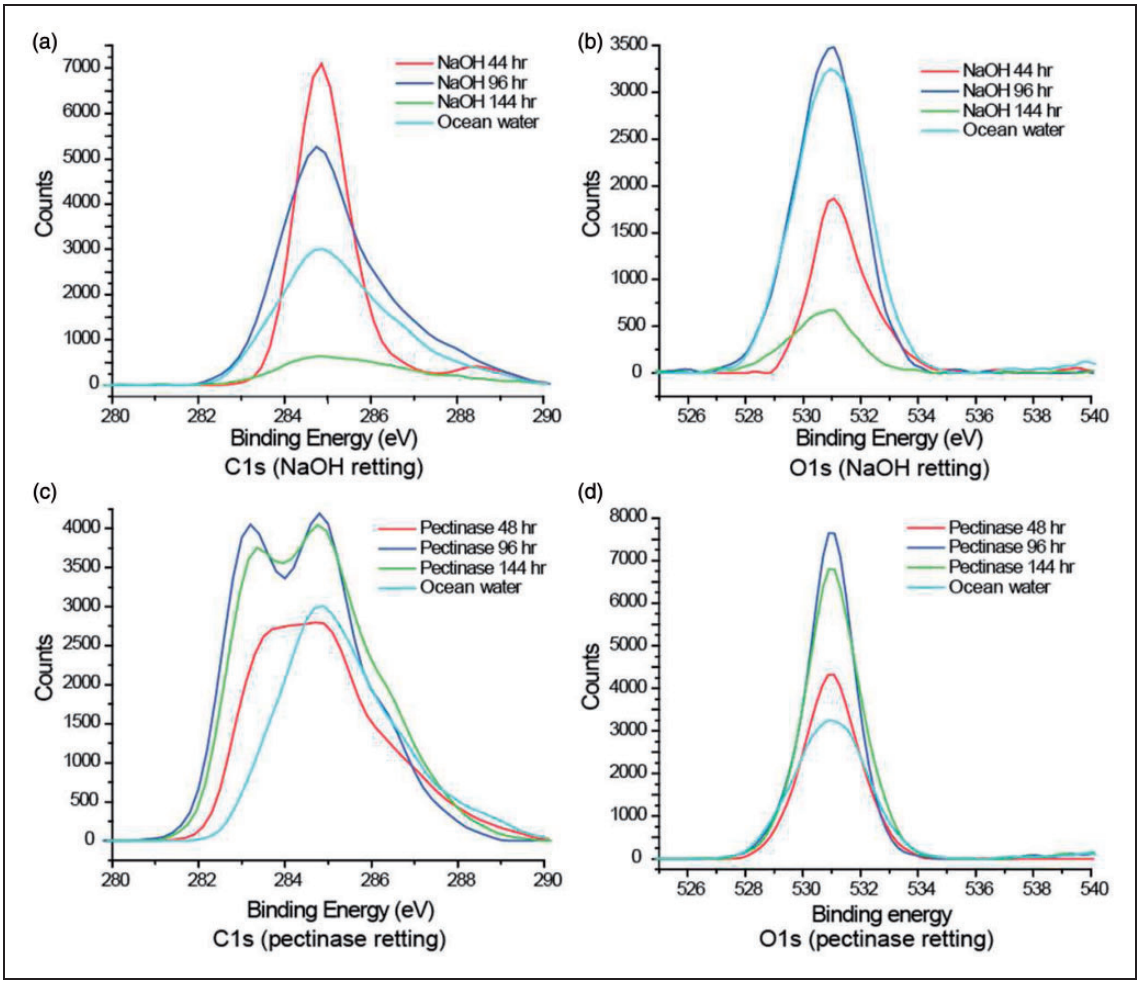

Figure 3. Carbon and oxygen regions of X-ray photoelectron spectroscopy (XPS) spectra in alkali- and enzyme-treated kenaf fibers. Spectra of the C1s (a) and O1s (b) region of XPS performed on alkali-retted fibers and spectra of the C1s (c) and O1s (d) region of XPS performed on pectinase-retted fibers. Red, blue and green lines represent the indicated duration of each treatment, and commercial fiber retted in ocean water (cyan) is included for comparison. (Color online only.)

(Figure 2(a)) and after 96 h of retting, considerable cell-wall remnants of non-fibrous cells remained attached to the fiber strands (Figure 2(c)). Only after 144 h of alkali retting were the fiber bundles well-separated and free of non-fiber debris (Figure 2(e)). All of the pectinase treatments (48, 96 and 144 h, Figures 2(b), (d) and (f), respectively) produced well-separated fiber bundles free of non-fiber debris, and equivalent to the commercial control that was retted in ocean water (Figure 2(g)).

The remnants of non-fiber cells with alkali retting compared to pectinase retting can be understood with respect to the cell-wall architecture of regular cells and fiber cells, and the retting agent's mode of action. Non-fiber cell walls are thinner and have little or no lignin functioning as a matrix to embed the cell-wall carbohydrates. The cell walls of fiber cells, on the other hand, are thicker and the carbohydrates are embedded in lignin, as evident from the intense blue autofluorescence observed in Figure 1.[25] Pectinase and water retting are more active against and more selective for non-fiber cells because the carbohydrates

Table 1. Elemental composition of carbon and oxygen as determined by X-ray photoelectron spectroscopy

	C1s	O1s	O/C ratio
NaOH 44 h	83.3%	16.7%	0.20
NaOH 96 h	72.1%	27.9%	0.38
NaOH 144 h	72.5%	27.5%	0.38
Pectinase 48 h	66.0%	34.0%	0.51
Pectinase 96 h	64.0%	36.0%	0.56
Pectinase 144 h	65.7%	34.3%	0.52
Ocean water	68.3%	31.7%	0.46

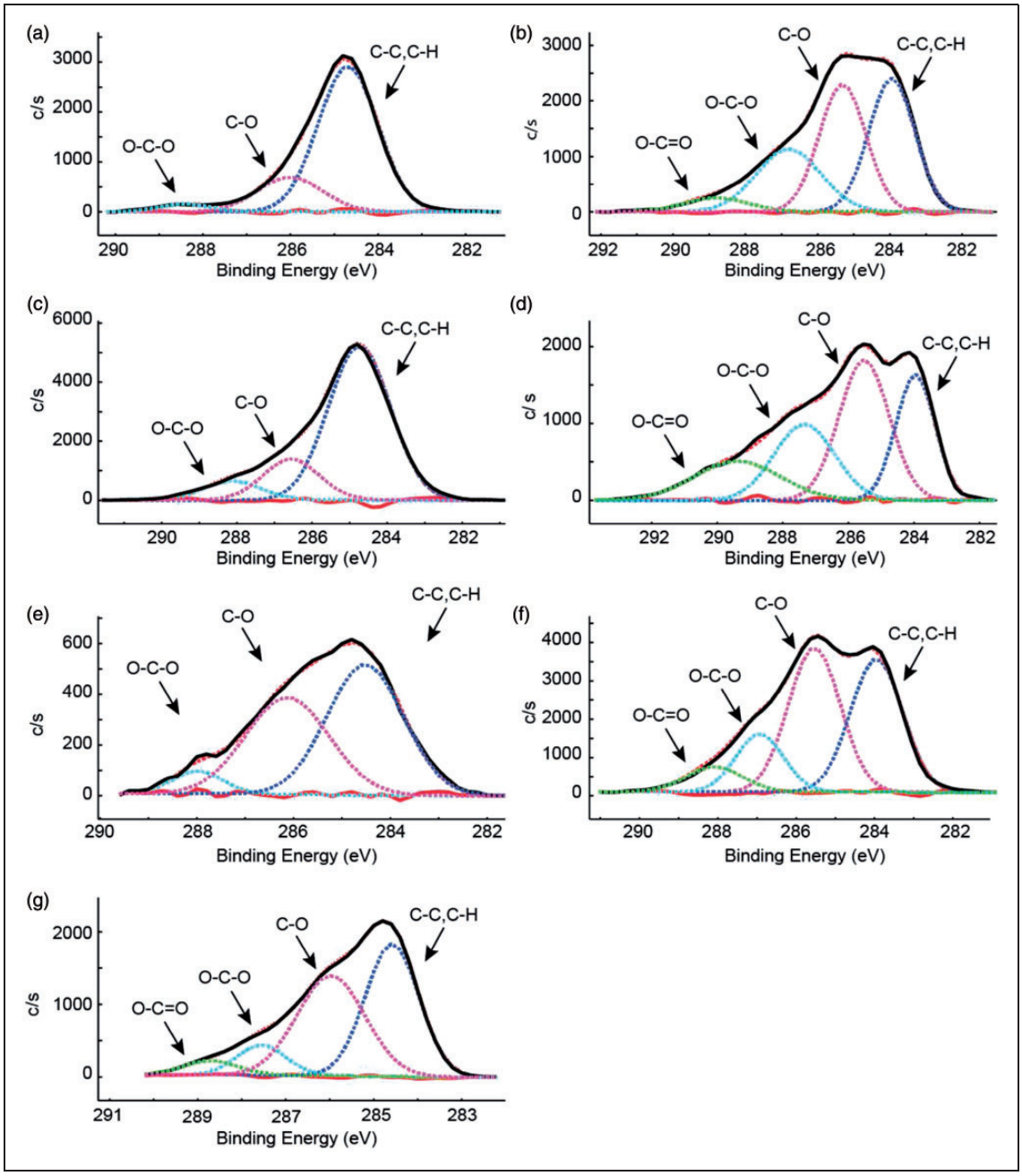

Figure 4. Comparison of deconvoluted carbon 1 s peaks. Retting treatment and duration were with 2% NaOH (w/v) ((a), (c), (e)) for 44 h (a), 96 h (c) and 144 h (e); and with 0.25% pectinase solution (v/v) ((b), (d), (f)) for 48 h (b), 96 h (d) and 144 h (f). For comparison, fibers from a commercial source retted in ocean water are shown (g). Colored lines represent the following: solid black, measured C1s peak; dashed red, total of the deconvoluted peaks; dashed green, deconvoluted O-C=O peak; dashed cyan, deconvoluted O-C-O peak; dashed magenta, deconvoluted C-O peak; dashed blue, C-C and C-H peak; solid red, difference between measured C1s peak and the sum of deconvoluted peaks. (Color online only.)

are more accessible to the enzymes for digestion; the fiber cells are less affected because the thickness of the walls and the lignin polymer provide resistance to degradation. Conversely, alkali permeates the cell wall and acts more indiscriminately against the cell-wall polymers.

Surface chemistry

The chemical composition at the fiber surface is crucial in determining the interfacial interaction with a polymer matrix in a composite material, and knowledge of the functional groups present on the fiber surface would

Table 2. C1s component intensities of alkali, pectinase and ocean water-retted fibers

	C1 (C-C,C-H)	C2 (C-O)	C3 (O-C-O)	C4 (O-C=O)
NaOH 44 h (eV)	284.69	286.01	288.40	–
	77.38%	18.44%	4.19%	
NaOH 96 h (eV)	284.79	286.55	288.12	–
	71.80%	19.24%	8.97%	
NaOH 144 h (eV)	284.51	286.13	287.99	–
	52.17%	38.62%	9.20%	
Pectinase 48 h (eV)	283.95	285.31	286.80	288.81
	39.52%	37.81%	18.54%	4.13%
Pectinase 96 h (eV)	283.95	285.52	287.34	289.38
	32.98%	36.82%	19.98%	10.20%
Pectinase 144 h (eV)	284.11	285.69	287.09	288.25
	36.92%	40.02%	16.10%	6.97%
Ocean water (eV)	284.58	285.97	287.55	288.71
	47.94%	36.09%	10.88%	5.09%

aid in the choice of polymer. The cell walls of bast fibers are composites of primarily lignin and long-chain carbohydrates of cellulose, hemicelluloses and pectins. Lignin is a hydrocarbon polymer consisting of both aliphatic and aromatic functional groups, and has a low oxygen:carbon ratio (O/C ratio) compared to cell-wall carbohydrates. Carbohydrates have higher O/C ratios due to the increased number of OH, CHO and COOH functional groups.[26] These functional groups can be utilized for surface modifications of the fiber by choosing suitable linking molecules between the fiber surface and the polymer matrix. Therefore, XPS and Raman spectroscopy were conducted to assess the chemical composition at the fiber surfaces.

The results of XPS are shown in Figure 3 with the extracted O/C values in Table 1. The low O/C ratio of alkali retted fibers relative to pectinase retted fibers argues that alkali-retted fiber has more lignin and fewer functional groups on the surface. The higher O/C ratio of pectinase-retted fiber argues that there is less surface lignin and more exposed carbohydrate with groups which can be used for functionalization (Table 1). The C1s spectra at 283 eV correspond to C-C and C-H bonding. This peak is observed in all of the pectinase retted samples along with C-O bonding. When we measure the intensity of carbon 1s and oxygen 1s peaks, the ratio of O/C in pectinase retted samples are higher indicating more oxygen content on the surface of the pectinase retted fiber.

Figure 4 shows the peak fitting analysis for the individual C1s peaks and the C1s component intensities are provided in Table 2. With alkali retting, the fiber surfaces appear covered with lignin as evident from the corresponding higher C-C and C-H intensities, whereas pectinase and ocean water retting results in fiber surfaces with more C-O and C = O functional groups indicating more exposed carbohydrate. These groups can be functionalized by acetylation, silylation and esterification, and thus pectinase and water retting enhances the feasibility of modifying fiber surfaces, relative to alkali retting.

To independently validate the XPS results, Raman spectroscopy was performed (Figure 5). The peak at 1621 cm^{-1} corresponds to symmetric aryl ring stretching of lignin[27,28] and the intensity of this peak reduced considerably as the retting duration increases from 48 to 144 h for all samples. The peak at 2960 cm^{-1} is due to asymmetric C-H stretching of the O-CH_3 group from lignin. This also reduced significantly as retting duration increased. We speculate that the peak splitting or shoulder band at 1621 cm^{-1} for the 144 h retted samples could be due to ring conjugated C=C stretching of coniferyl alcohol and C=O stretching of coniferaldehyde in lignin polymers.[27,28] The method of retting affected the magnitudes of the decreases in peak intensity. In the ocean water-retted commercial sample, most of the lignin is preserved, whereas as with increased duration of alkali and pectinase treatment, lignin content reduced significantly. Pectinase retting resulted in a greater loss of lignin than alkali retting.

Storage modulus (E') of retted fibers

Storage modulus values directly relate to structural integrity and elastic response, and have correlated to the sound absorption properties of materials.[29] Figure 6 shows the storage modulus E' values of the enzymatic, alkali and ocean water-retted commercial sample. The results show that alkali-retted fibers have the lowest storage modulus relative to the enzymatic and ocean water-retted fibers. We previously investigated *Sesbania herbacea* fibers[19] with similar trends. The decrease in the E' values for alkali-retted fibers

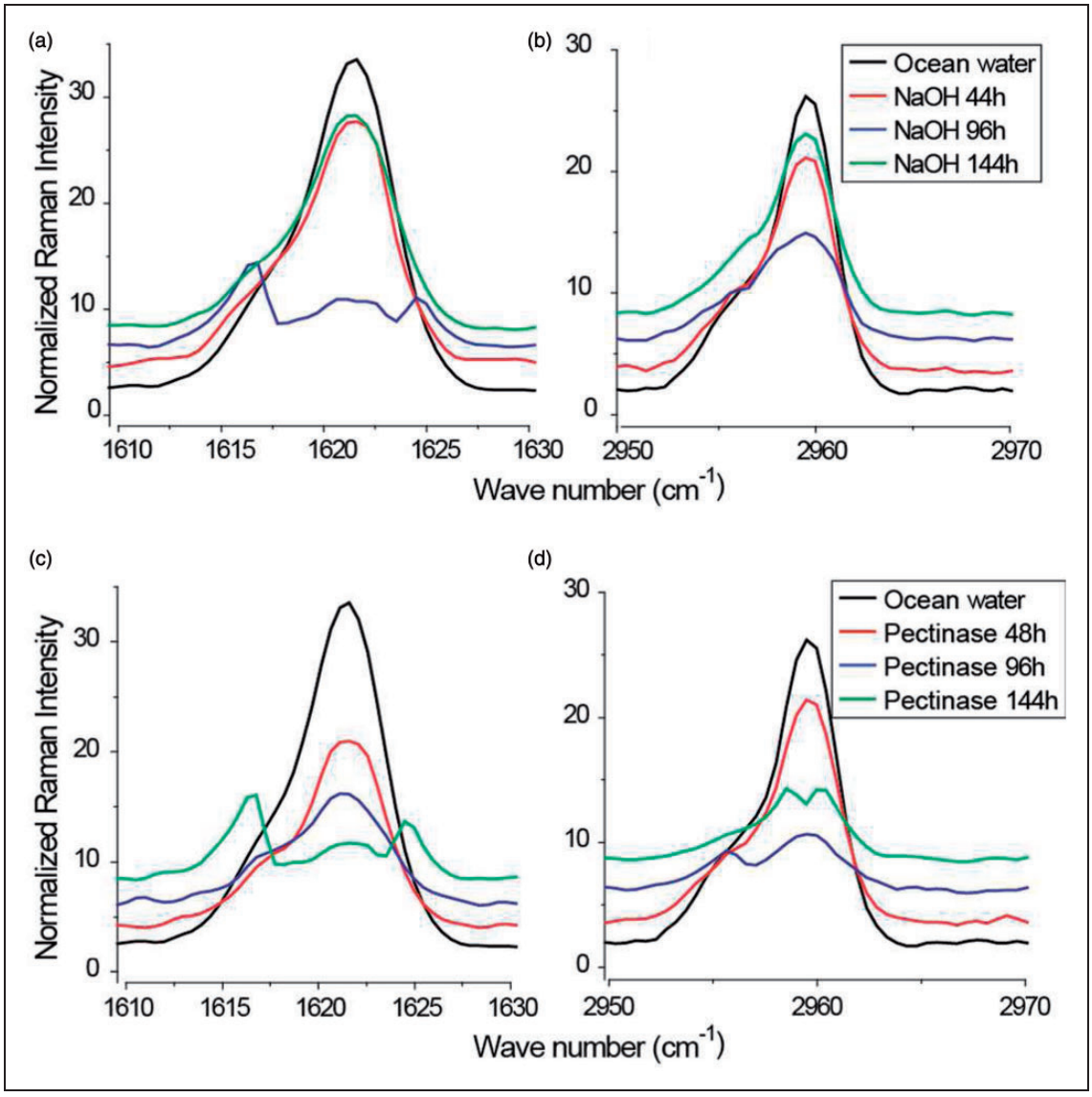

Figure 5. Raman spectra of alkali, pectinase and ocean water-retted fibers. Raman spectra of alkali-retted fibers in the region of 1621 (a) and 2960 (b) cm^{-1}. Raman spectra of pectinase-retted fibers in the region of 1621 (c) and 2960 (d) cm^{-1}. The peak at 1621 cm^{-1} corresponds to symmetric aryl ring stretching of lignin and the peak at 2960 cm^{-1} is due to asymmetric C-H stretching of O-CH3 group from lignin. Red, blue and green lines represent the indicated duration of each treatment, and commercial fiber retted in ocean water (black) is included for comparison. (Color online only.)

is likely due to disruption of the porous architecture of the fibers during alkali retting. During alkali retting, the cross-sectional, honeycomb architecture of fibers deteriorates considerably with even the shortest incubation tested (Figure 1), but there is modest increase in E' with longer retting times. The commercial standard and the enzymatically retted fibers had storage modulus values exceeding the alkali-retted fibers as much as three fold. The preservation of the fiber structural integrity during retting likely benefits the E' values. With enzymatic retting, there is a substantial E' drop from 48 to 96 h, but no significant difference between 96 and 144 h. The phenomena of no change between 96 and 144 h occurs for both the NaOH and pectinase-retted fibers, indicating that the initial chemistry between the retting fluid and the fiber affects the fiber moduli substantially but for longer times there is no substantial change. For NaOH, the moduli have close to similar values with time, which are all lower than the pectinase values initially. The absence of a change in storage modulus for the enzymatic treatment above 96 h is reflective of both the inactivity of the enzymes after 96 h leading to minimal further retting. In the case of the alkali retting,

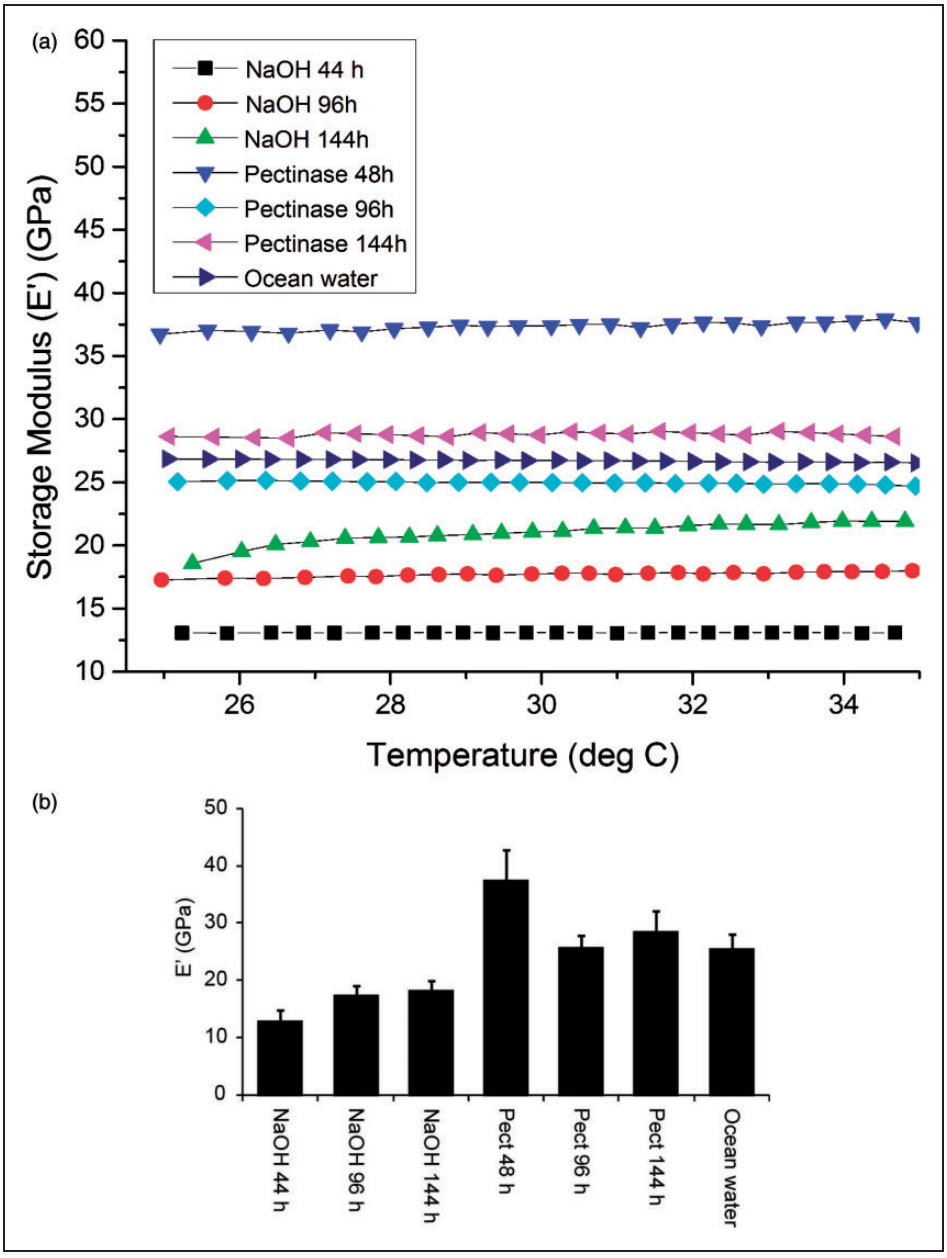

Figure 6. Comparison of storage modulus (E') for fibers subjected to the indicated retting treatment; Pect: pectinase; variation is represented by standard error; $n = 10$. (a) Corresponds to dynamic mechanical analysis measurements whose averages are numerically plotted in (b).

the loss of pectins has likely occurred by the 96 h, leaving no more reduction of storage moduli in the fibers.

Carbohydrate composition of retted fibers

To further analyze the impacts of retting strategy on fiber chemistry, fibers were subjected to acid hydrolysis to release the monosaccharide constituents of the fiber carbohydrates, and the neutral sugars were quantified by high performance anion exchange chromatography with pulsed-amperometric detection (HPAEC-PAD; Figure 7). Relative to the unretted control, arabinose and galactose levels dropped from 5.1% and 2.6%, respectively, to less than 1% of total carbohydrate with alkali, pectinase, and ocean-water retting (Figure 7a). These neutral sugars, along with galacturonic acid, are found predominantly in pectins,[25] and this indicates that all treatments effectively dissolve or digest pectin carbohydrates. Mannose (Figure 7a) is a

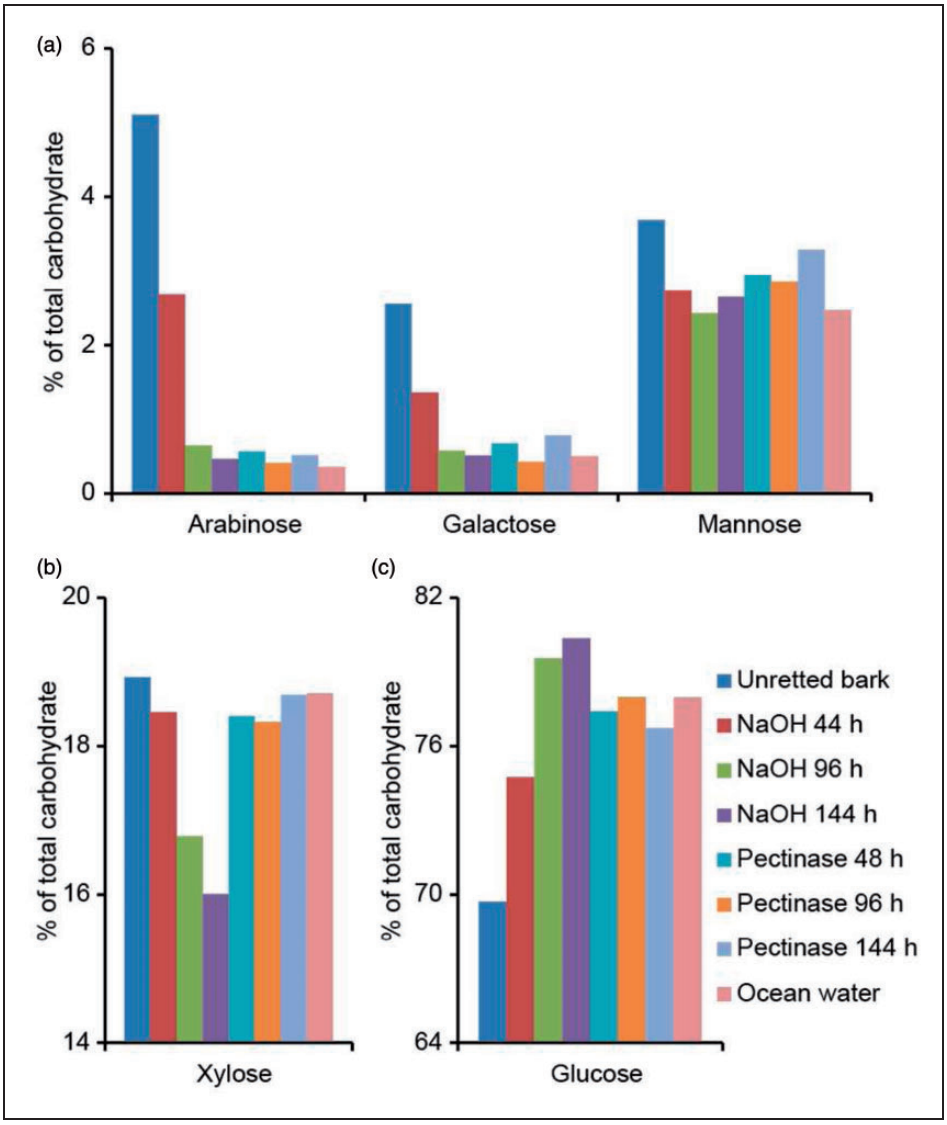

Figure 7. Percent of individual neutral sugar monomers relative to total neutral sugars hydrolyzed from each fiber sample. Neutral pectin sugars, arabinose and galactose, and the minor hemicellulose sugar mannose (a); prominent hemicellulose sugar xylose (b); and glucose (c) of cellulose and some hemicelluloses. Note that the percent abundance (*y*-axis) is presented with different scales for clarity; the total neutral sugar for each fiber sample is 100%. Retting treatments and duration are indicated by color, and an unretted bark sample containing both fiber cells and non-fiber cells is included for comparison. Values presented are the average of two measurements.

minor constituent of hemicelluloses and shows a minor drop among all treatments relative to the unretted control. Xylose (Figure 7(b)), however, is prominent in hemicelluloses and therefore a more informative indicator of retting impact on this group of carbohydrates.[25] Xylose content, and thus hemicellulose content, decreased substantially with longer alkali retting but was virtually unaffected by pectinase and ocean water retting (Figure 7(b)). This is expected since hemicelluloses are known to be extractable with NaOH, but are poorly recognized by pectinase enzymes[25] and may be less accessible to microbes because of the close association with the cellulose microfibrils and lignin. Importantly, NaOH-mediated loosening or release of hemicelluloses from the cell-wall matrix likely contributes to the inferior storage modulus (E') values observed (Figure 6), and to the occlusion of the central pores in the fiber bundles (Figure 1). Cellulose is a polymer of pure glucose, and glucose is also a prominent component of some hemicelluloses. Glucose is thus the major sugar of the fibers and forms a greater percentage of the total

residual sugar, since the other classes of cell-wall carbohydrate are dissolved or digested during the retting procedures (Figure 7(c)).

Conclusion

Experiments were conducted to characterize the mechanical properties and surface functional group availability in kenaf bast fibers retted with alkali solutions and pectinase preparations, and compared to a commercially available fiber source retted by the natural microbial populations of ocean water. It is evident that pectinase treatment effectively removes pectins and lignin from kenaf fiber surfaces, while leaving a higher proportion of exposed carbohydrate functional groups. Alkali treatment similarly removed pectins, but also removed hemicellulose, and resulted in exposure of more lignin-derived functional groups. Pectinase treatment yielded fibers with superior mechanical properties, and the higher E' for pectinase over the alkali-retted fibers can be attributed to the retention of fiber structural integrity. From the microscopic cross-sectional view of the fibers, it is observed that alkali-retted fibers lose the central pore of the fiber cells, thereby reducing the modulus values compared to pectinase and ocean water retting. The inferior structural and mechanical properties of the alkali-retted fibers are likely associated with loss and disruption of hemicellulose in the cell-wall matrix. The surface morphology of fibers were compared, and it was found that pectinase retting resulted in uniformly smooth surfaces comparable to that of ocean water retting, while shorter alkali treatments retained remnants of non-fiber cell walls. An interesting inversion in trends for E' over retting time was observed when comparing the alkali-retted fibers to the enzymatic retted fibers. In the alkali-retted fibers the E' increases slightly over time, while in the enzymatic retted process the E' decreased over time. We postulate that the lignin loss over time in NaOH led to higher fiber compaction and this density increase across the cross-section would result in increased E' values. For the pectinase fibers with preservation of the porous structure, there is no change in density; thus, loss of lignin and chemical constituents would cause a loss of E' over retting time. In conclusion, we observe that pectinase retting yields more consistent and superior quality fibers with higher mechanical properties as well as availability of functional groups on the surface capable of functionalization to influence the fiber–matrix interface of composites. Pectinase retting also has a shorter duration time, allows greater control over the retting process, and is more suited to large-scale production. However, these attributes must be weighed against enzyme costs for commercial feasibility and we are also exploring the use of defined microbial consortia for equivalent gains.[30]

Acknowledgments

The authors thank the members of their respective laboratories (BGA, NDS and CLW) for technical assistance. The authors acknowledge the peer reviewers for insightful comments, particularly on the storage moduli-pectin loss analysis.

Funding

This work was supported by the National Science Foundation (grant numbers CMMI 1031828, DBI 1126205 and PFI 1114389).

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