Alkali and Peroxide Bleach Treatments on Spring Harvested Switchgrass for Potential Composite Application

Eugene Enriquez,[a,b] Amar K. Mohanty,[a,b,*] and Manjusri Misra [a,b,*]

Natural fibers are desirable in composite applications for their sustainability. However, improving upon the interfacial adhesion between the fiber and matrix is a major challenge. Chemical surface modification is a method used to improve compatibility of the fiber by exposing or adding functionalities to the surface, and removing non-cellulosic components in order to enhance mechanical and thermal properties. Switchgrass, an abundant natural fiber, has potential for use as a reinforcing material in composite applications. Surface modifications were conducted on switchgrass *via* alkali and peroxide bleaching treatments in order to remove surface impurities and create a rougher surface, as observed in scanning electron micrographs. Fourier transform infrared spectroscopy and compositional analysis showed that non-cellulosic components were reduced following the alkali and bleach treatments. Reduction of hemicellulose and lignin improved thermal stability by increasing the onset temperature of degradation from 258 °C to 289 and 281 °C for alkali and bleach treatments, respectively. The crystallinity index (CI) of untreated and treated fibers was calculated from x-ray diffraction analyses. An increase of 48% and 38% for the alkali and bleach treated fibers, respectively, was seen in the CI, compared to the untreated switchgrass. The surface of switchgrass was successfully modified using alkali and peroxide bleach treatments for composite applications.

Keywords: Alkali Treatment; Bleach Treatment; Peroxide Bleaching; Switchgrass; Natural Fibers; Surface Modification

Contact information: a: Bioproducts Discovery and Development Centre (BDDC), Department of Plant Agriculture, University of Guelph, 50 Stone Road East, Guelph, ON, N1G 2W1, Canada; b: School of Engineering, University of Guelph, 50 Stone Road East, Guelph, ON, N1G 2W1, Canada;
** Corresponding authors: mohanty@uoguelph.ca and mmisra@uoguelph.ca*

INTRODUCTION

Environmental concerns, such as increased waste and greenhouse gas emissions, have been a major topic of debate as society continues to shift its focus towards more sustainable methods and materials. Renewability, lower costs, density compared to synthetic fibers, and biodegradability are some of the major advantages of using natural fibers as a reinforcement or filler material in polymer composites (Bismarck *et al.* 2005). A significant amount of research has been conducted on the utilization of natural fibers for biocomposite applications (Faruk *et al.* 2012). Despite the attractiveness of natural fibers for composite uses, poor compatibility between the fiber and matrix, limited availability of reactive sites on the fiber surface, and a high level of moisture absorption due to inherent hydrophilicity all have major effects on the performance of natural fiber composites (Obi Reddy *et al.* 2013; Indran and Raj 2015). Since a large variety of natural fibers exists, the composition of their chemical constituents (cellulose, hemicellulose, and lignin) vary from plant to plant, causing variability in the performance of the materials (Faruk *et al.* 2012). Increased compatibility and consistent natural fiber properties for polymer composite applications can be achieved by modifying the surface of the fiber to improve the mechanical, physical, and thermal properties (Li *et al.* 2007). Surface modifications, achieved through alkali and peroxide bleach treatments, are capable of improving the interfacial adhesion of the natural fibers to the polymer matrix by increasing surface roughness and allowing for better physical interlocking (Mohanty *et al.* 2001).

The alkali treatment process works by removing hemicellulose, lignin, wax, oils, and other surface impurities. Alkali concentration, duration, and temperature are factors that determine the removal of non-cellulosic components during the alkali treatment process (Li *et al.* 2007). During treatment, cellulose begins to split within the fiber, rearrange, and pack closely together in order to relieve internal strain. This produces a rougher fiber surface morphology, allowing for improved mechanical interlocking with the polymer matrix. In addition, the number of hydroxyl groups on the surface are increased, which can result in advantageous chemical interactions between the fiber and polymer (Ridzuan *et al.* 2016). A number of natural fibers such as agave (El Oudiani *et al.* 2012), alfa (Borchani *et al.* 2015), bamboo (Das and Chakraborty 2006; Liu and Hu 2008; Das and Chakraborty 2008; Zhang *et al.* 2015), century fiber (Obi Reddy *et al.* 2013), hemp (Mwaikambo and Ansell 2002; Liu *et al.* 2013), jute (Mwaikambo and Ansell 2002; Saha *et al.* 2010), *Prosopis jujiflora* (Saravanakumar *et al.* 2014), reed (Barman *et al.* 2014), sisal (Mwaikambo and Ansell 2002; Khan *et al.* 2012), kapok (Mwaikambo and Ansell 2002), and Indian grass (Liu et al. 2004) have been subjected to an alkali pretreatment before combining with polymer matrix. It was observed by several researchers (Mwaikambo and Ansell 2002; Das and Chakraborty 2006; Liu and Hu 2008; Das and Chakraborty 2008; Saha *et al.* 2010; El Oudiani *et al.* 2012), that the sodium hydroxide concentration greatly affects the properties of the fibers. An increase of properties is reached at a certain concentration of sodium hydroxide and then falls with increasing concentrations. It was found that bamboo fibers exhibited a maximum change in mechanical properties (tensile and flexural strength and modulus) for 10 and 15% concentrations of sodium hydroxide (Das and Chakraborty 2008). However, when agave fibers were treated with concentrations greater than 2% sodium hydroxide, the tensile strength of the agave fibers began to decrease (El Oudiani *et al.* 2012). Thus, with appropriate alkali treatment parameters, mechanical, physical, and thermal properties of the fiber can be expected to enhance to a level desirable for composite applications.

Similarly to the alkali treatment of natural fibers, peroxide bleach treatment modifies the surface of natural fibers by removing non-cellulosic components, and improving upon the appearance of the fiber. The majority of natural fiber bleaching research has been conducted for the textile industry (Saheb *et al.* 1999; Subramanian *et al.* 2005; Imtiazuddin and Tiki 2015) and the pulp and paper industry (Li *et al.* 2005; He and Wekesa 2006; He and Ni 2008), utilizing chlorine-based bleaches (sodium hypochlorite or calcium hypochlorite) and hydrogen peroxide (Saheb *et al.* 1999).

Limited research has been conducted on bleaching lignocellulosic materials, especially for composite applications.

The peroxide bleaching of natural fibers such as kenaf (Salam *et al.* 2007; Razak *et al.* 2014), cornhusk (Salam *et al.* 2007), jute (Salam 2006; Imtiazuddin and Tiki 2015), oil palm empty fruit bunch (Marwah *et al.* 2014), and oil palm mesocarp (Then *et al.* 2015) fibers has been previously examined. Bleaching kenaf and cornhusk fibers produced a high whiteness index while still maintaining the tensile properties of the fibers (Salam *et al.* 2007). In consensus, it was determined that peroxide bleaching yields a whiter and brighter fiber by eliminating non-cellulosic components.

Switchgrass (*Panicum virgatum* L.) is a promising material because of its high environmental tolerance (heat, cold, and drought conditions), large production yield, ability to grow on marginal lands, minimal dependence on water and nutrients for growth, and benefits to the environment (Pasangulapati *et al.* 2012). Research has been conducted on switchgrass for bioethanol production, thermochemical conversion, pulping and paper making, and composite applications (Keshwani and Cheng 2009). Alkali pretreatments have been implemented on switchgrass in order to make carbohydrates more readily available for enzymatic hydrolysis (Keshwani and Cheng 2009). Similarly, the bleachability of switchgrass has also been studied for the pulp and paper industry (Radiotis *et al.* 1999). The purpose of this study was to apply an alkali and peroxide bleach treatment to switchgrass in order to prepare a natural fiber for composite applications with improved compatibility and appearance.

EXPERIMENTAL

Materials

Nott Farms, Ltd. (Clinton, ON, Canada) supplied switchgrass harvested in the spring of 2012, and milled to approximately 4 to 8 mm. Sodium hydroxide, glacial acetic acid, and hydrogen peroxide were purchased from Fisher Scientific. Sodium silicate, sodium persulfate, magnesium sulfate, and a non-ionic surfactant Span80 were purchased from Sigma Aldrich.

Sample Preparation

Prior to alkali and peroxide bleach treatments, switchgrass was sieved through a 1 mm sieve using a Ro-Tap sieve shaker (WS Tyler, OH, USA) for 10 min. Fibers greater than 1 mm remaining on top of the sieve were collected and subjected to the chemical surface treatment.

Alkali treatment

This study used an alkali solution of 5 weight to volume percent (wt./V%) on the sieved switchgrass with a liquor ratio of 1:20 for 24 h at room temperature. Upon completion of the alkali treatment, the fibers were rinsed 3 times with 1000 mL of distilled water. The fibers were then washed with 1000 mL of a 1 volume to volume percent (V/V%) solution of glacial acetic acid for 1 h in order to neutralize any sodium hydroxide on the fibers. After this, distilled water washing was continued until a pH of 7 was reached. After the washing process, the treated fibers were left to air dry for 3 days in a fume hood, then dried in an oven set at a temperature of 80 °C for at least 2 days prior to characterization.

Peroxide bleach treatment

In this study, a bleach solution consisting of 3.475 wt./V% sodium silicate, 3.0 wt./V% sodium hydroxide, 0.5 wt./V% sodium persulfate, 0.5 V/V% Span80 (a non-ionic surfactant), 0.025 wt./V% magnesium sulfate, and 5.0 V/V% hydrogen peroxide was used on the switchgrass. A bleach liquor ratio of 1:15 was employed in order to change the physical appearance of the fibers by partially eliminating non-cellulosic components. The switchgrass was subjected to the bleach liquor for 3 h at room temperature, at which point the treated fibers were rinsed with 1000 mL of distilled water 3 times before being washed with a 1 V/V % solution of glacial acetic acid for 1 h. After neutralizing the fibers with the acid solution, distilled water was again used on the fibers until a pH of 7 was reached. Once the desired pH was achieved, the treated fibers were left to air dry for 3 days in a fume hood, and then placed in an oven set a temperature of 80 °C for at least 2 days prior to characterization.

Characterization Methods

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) (Nicolet 6700, Thermo Fisher Scientific, USA) was used to observe any changes in the chemical groups found in the switchgrass. Individual fibers were used to determine the specific wavenumbers associated with characteristic peaks of the sample. The transmittance of the untreated and treated switchgrass was scanned 32 times within a range of 4000 to 500 cm^{-1}.

Compositional analysis

Compositional analysis was conducted by SGS Agrifood Laboratories (Guelph, Ontario, Canada) to determine the cellulose, hemicellulose, and lignin contents of the untreated and treated switchgrass. The compositional analysis of the fibers was performed using wet chemistry according to specified methods (highlighted in square brackets) in order to determine the acid detergent fiber (ADF) [AOAC 973.18], neutral detergent fiber (NDF) [AOAC 2002.04], and lignin [AOAC 973.18] content. The cellulose and hemicellulose contents can be derived from the ADF, NDF, and lignin values characterized because the ADF provides insight into the cellulose and lignin content, and NDF provides a value for the ADF portion, which includes the hemicellulose content. Therefore, the cellulose content can be calculated by subtracting the lignin determination from the ADF value. Similarly, the hemicellulose content can be calculated by subtracting the ADF from the NDF value.

Thermogravimetric analysis

A thermogravimetric analyzer (TGA), (TA Q500, TA Instruments, USA) was used to measure the thermal stability of the treated and untreated switchgrass. Three replicates of 5 to 10 mg of material were subjected to a heating rate of 20 °C/min from 30 to 800 °C. The test was conducted in a nitrogen environment with a purge and balance flow of 40 and 60 mL/min, respectively.

Scanning electron microscopy

The morphological properties of the fibers were examined using scanning electron microscopy (SEM) (Phenom Pro X, PhenomWorld, Netherlands) at 1000x magnification with an accelerating voltage of 15 kV. The SEM images helped to understand the effects alkali and peroxide bleach treatments had on the surface of the switchgrass. A thin conductive layer of gold was deposited onto the surface of the sample before examination.

X-ray diffraction

XRD analysis was performed by the Soldatov Lab at the University of Guelph (Guelph, Ontario, Canada). The untreated and treated switchgrass samples were mounted onto a glass fiber using vacuum grease. A single-crystal diffractomer (SuperNova Agilent) was used to study the samples at room temperature. The radiation source for the diffractometer was from a microfocus CuKα (λ = 1.54184 Å) using an Atlas CCD detector. A one-dimensional powder pattern was generated from the XRD images that were collected from a goniometer using ϕ-scans from five different angular positions within a 2θ range of 5 to 140°. CrysAlisPro software (Agilent Technologies 2013) was used to process the XRD images collected.

The crystallinity index (CI) was determined through XRD analysis using Segal's empirical method according to Eq. 1 (Segal *et al.* 1959),

$$CI = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \tag{1}$$

I_{002} is the maximum intensity for the 002 lattice plane of the cellulose structure found at 2θ=21.75°, and I_{am} is the intensity value of the amorphous region found at 2θ=18.52°.

RESULTS AND DISCUSSION

Effects of Surface Treatment on Switchgrass

Chemical treatments such as alkali and peroxide bleach treatments are often used in the removal of lignin, hemicellulose, and other surface impurities. Sodium hydroxide is capable of solubilizing the surface impurities and other non-cellulosic components present in switchgrass (Bismarck *et al.* 2005). Cellulose fibrils that cause a rough fiber surface that is beneficial for composite applications are uncovered following the removal of non-cellulosic components (Mwaikambo and Ansell 2002). Strong alkali solutions are capable of altering the crystal structure of cellulose, causing an irreversible conversion from cellulose I to II, due to the changes in crystallite length and packing order (El Oudiani *et al.* 2012). Most of the structural changes that happen to the fiber have been reported to occur after neutralization and drying (Ozturk *et al.* 2009). Alkali solutions cause swelling of the fiber by cleaving hydrogen bonds and rearranging the configuration, which in turn reduces the crystallinity. However, the neutralization and drying process changes the porosity and increases crystallinity after regenerating the cellulosic fibers (Ozturk *et al.* 2009).

The effects of alkali treatment on switchgrass can be seen in Fig. 1. Chlorophyll, the compound which provides natural fibers with a green color, is degraded by alkaline solutions (Elenga *et al.* 2013). Therefore, the alkali treatment enhanced the yellow color of switchgrass due to a decrease in the green chromophores of the natural fiber.

Fig. 1. Images of A) untreated switchgrass, B) alkali-treated switchgrass, and C) peroxide bleach-treated switchgrass

The peroxide bleaching process performed under alkaline conditions provides effects similar to those of alkali treatment while effectively bleaching the natural fibers. Under alkaline conditions, hydrogen peroxide dissociates into hydrogen (H^+) and perhydroxyl (^-OOH) ions, as seen in Fig. 2 (Xiang 1998). The perhydroxyl ion is the chemical species responsible for the bleaching effect on natural fibers because it is a strong nucleophile (Xiang 1998). However, hydrogen peroxide can decompose into other compounds which can reduce the brightening capabilities of the solution. Due to the possibility of hydrogen peroxide decomposition under basic conditions, additives such as sodium silicate and magnesium sulfate are added to stabilize the bleaching solution (Xiang 1998).

$$\underset{\text{Hydrogen Peroxide}}{\mathrm{HOOH}} \rightleftharpoons \underset{\text{Perhydroxyl Anion}}{\mathrm{H}^{+} + {}^{-}\mathrm{OOH}}$$

Fig. 2. Dissociation of hydrogen peroxide

In conjunction with the alkali treatment, the bleaching process can solubilize and remove non-cellulosic components of the natural fibers while simultaneously providing a whitening effect. Lignin is the compound in natural fibers that gives it a brown color. The chemical structure of lignin is very complex, and no consistent configuration has been determined. However, it is known that lignin consists of several types of monomeric units, in which the main species are *p*-coumaryl alcohol, coniferal alcohol, and sinapyl alcohol, as presented in Fig. 3 (Lange *et al.* 2013).

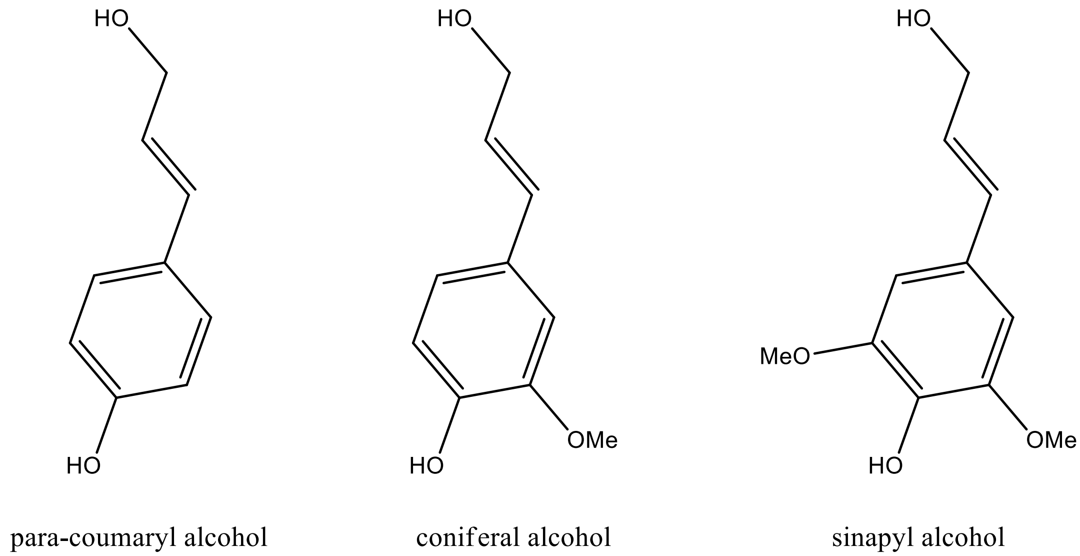

Fig. 3. Monomers of lignin: p-Coumaryl alcohol, coniferal alcohol, and sinapyl alcohol

Bleaching of natural fibers targets the components of lignin *via* oxidation. An example of the oxidation process for one monomer unit of lignin (*p*-coumaryl alcohol) is shown in Fig. 4, as a primer for the Dakin and Dakin-like reactions.

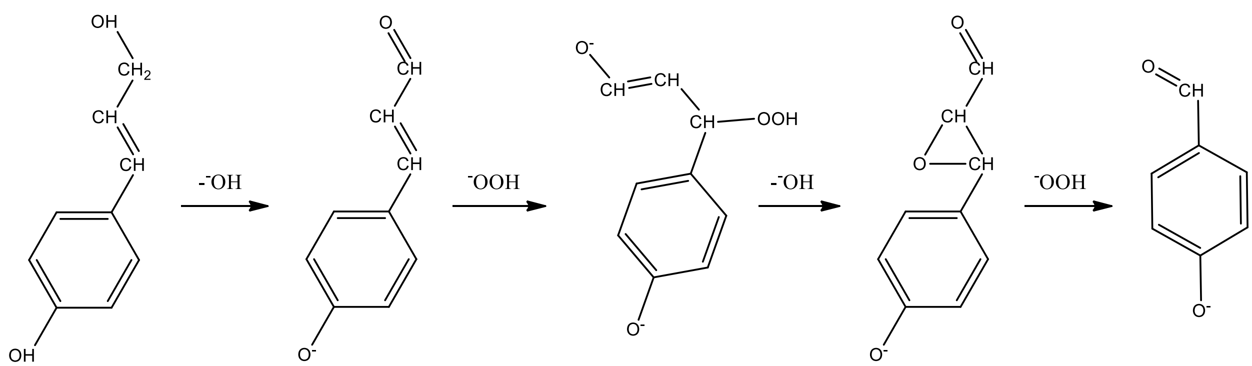

Fig. 4. Oxidation of *p*-coumaryl alcohol

Through oxidation and Dakin-like reactions (Fig. 5), hydrogen peroxide attacks the chromophores in lignin responsible for brown coloring by breaking down the main components of lignin into benzoquinone derivatives (Li *et al.* 2015). Dakin reactions are brought about by a series of rearrangements for the different monomeric structures of lignin by a sequence of electron exchanges with perhydroxyl ions.

The hydrogen peroxide bleaching changes the lignin chromophores into colorless compounds through a non-reversible reaction (Li *et al.* 2015). In Fig. 1, the bleaching effects of a hydrogen peroxide solution on switchgrass can be seen. The bleaching process improves upon the appearance of natural fibers by enhancing whiteness and removing other non-cellulosic components, which is beneficial for composite applications.

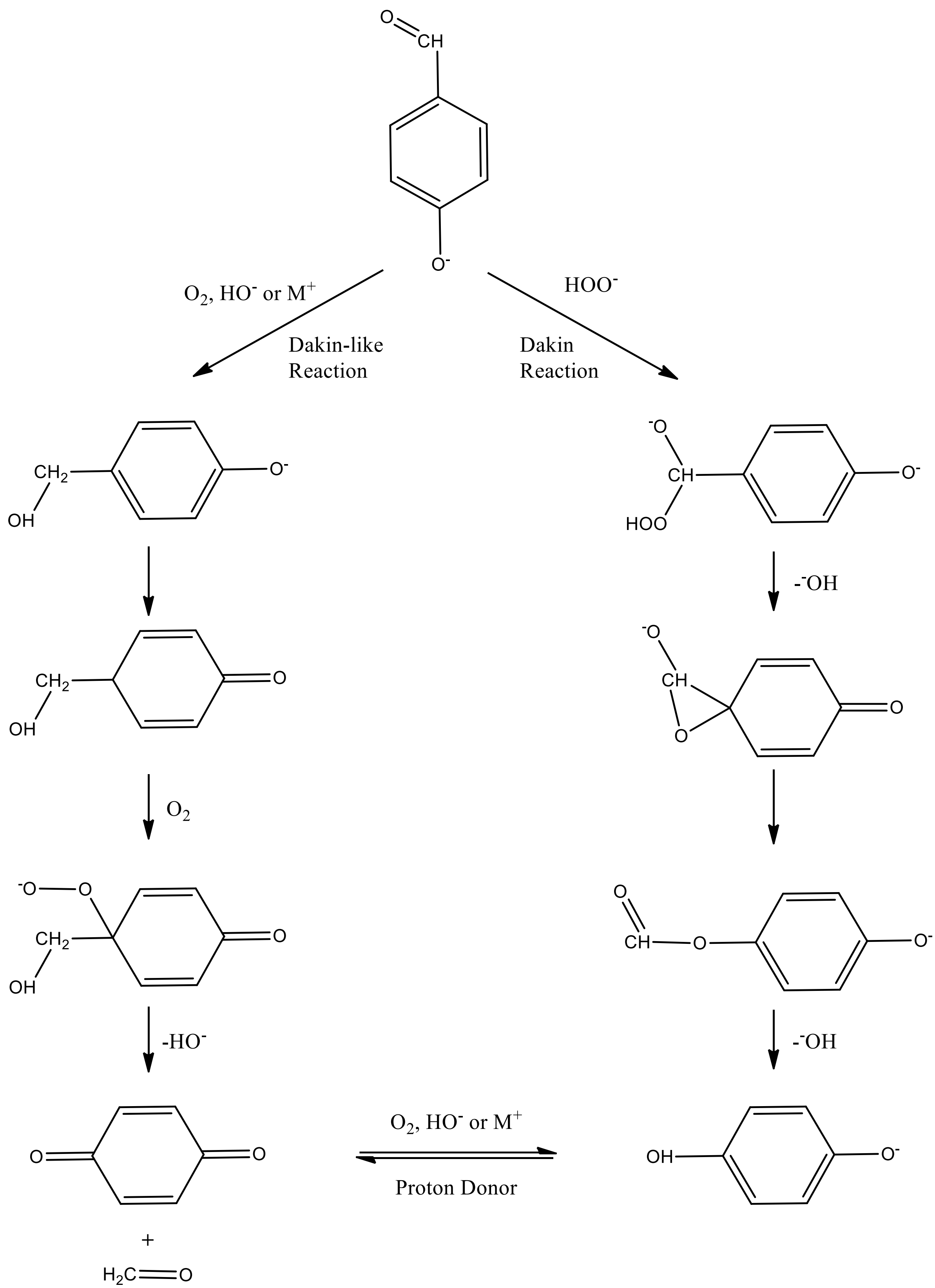

Fig. 5. Dakin and Dakin-like reactions of oxidized *p*-coumaryl alcohol

Fourier Transform Infrared Spectroscopy

The different chemical groups of switchgrass were determined using FTIR analysis, as presented in Fig. 6. The chemical groups discovered through FTIR analysis corresponded to the usual structures found in switchgrass such as cellulose, hemicellulose, lignin, and other non-cellulosic components.

The characteristic peaks of the untreated switchgrass can be seen at 3349 cm^{-1} for the hydroxy groups (-OH), 2917 cm^{-1} for the -CH vibrations of hemicelluloses, 1730 cm^{-1} for the -C=O groups corresponding to non-cellulosic components, 1510 $cm^{-1}$for the C=C of aromatic groups found in lignin, 1460 cm^{-1} for the CH deformation found in lignin, 1424 cm^{-1} for the CH deformation of lignin, 1238 cm^{-1} for the C-O-C groups found in hemicellulose, and at 1032 cm^{-1} for the C-O-C groups of cellulose (Pasangulapati *et al.* 2012; Borchani *et al.* 2015). The alkali and bleach treatments of switchgrass affected the characteristic peaks of non-cellulosic components through partial or complete removal.

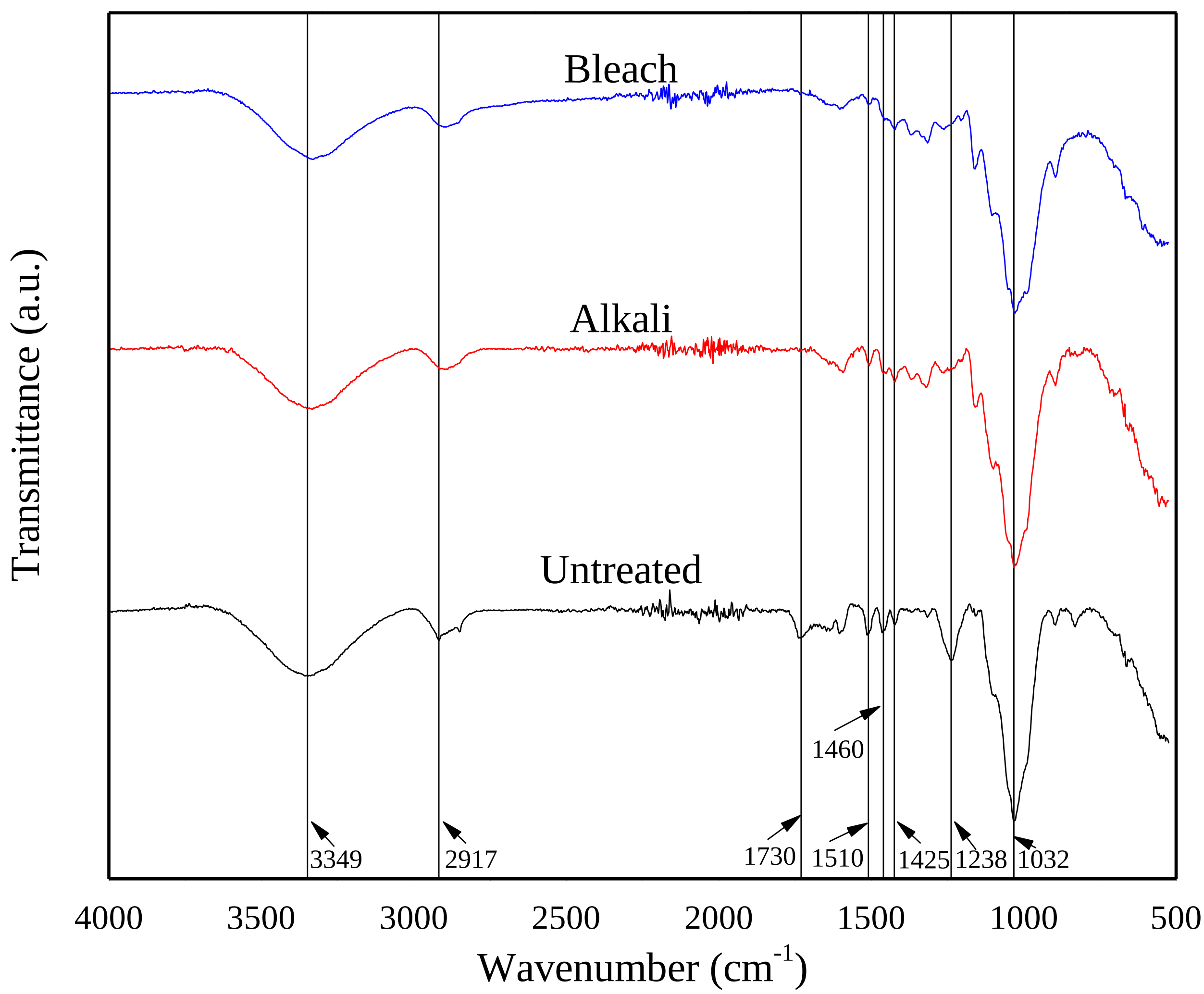

Fig. 6. FTIR spectra of untreated and treated switchgrass

Hemicellulose, waxes, oils, and other surface impurities are soluble in alkaline solutions. Therefore, the peaks found for untreated switchgrass at 2917 and 1730 cm^{-1} changed. The surface treatments caused the peak at 2917 cm^{-1} to reduce in intensity and broaden, indicating a partial removal of hemicellulose. Similarly, the peak at 1730 cm^{-1} completely disappeared, indicating the removal of structures containing a carboxylic group. A similar disappearance of the carboxylic groups' peak has been previously observed following alkali treatments of hemp, sisal, jute, and kapok fibers (Mwaikambo and Ansell 2002). This was attributed to the deesterification reaction that occurred in the presence of an alkaline solution.

The untreated switchgrass had three distinct peaks corresponding to lignin at 1510, 1460, and 1425 cm^{-1}. After the alkali treatment, the characteristic peaks for lignin were still visible and fairly distinct. Lignin can be easily oxidized, and it is soluble in hot alkali solutions (Bismarck *et al.* 2005). In this study, because the alkali treatment of switchgrass was conducted at room temperature (~23 °C), lignin removal was not accomplished. However, the peroxide bleaching was effective in reducing the lignin content of switchgrass. As can be seen in Fig. 4, the reaction schematic for the oxidation of the monomeric components of lignin demonstrates that lignin can be removed or altered by way of a peroxide bleaching process. The FTIR spectra for the bleach treated switchgrass show that the peak at 1510 cm^{-1} significantly decreased, and the peak at 1460 cm^{-1} was almost indistinguishable, as it became a shoulder for the 1410 cm^{-1} peak. Alkali treatment was capable of removing hemicellulose and other surface impurities. The peroxide bleaching process was able to reduce and remove more non-cellulosic components such as lignin.

Compositional Analysis

The main constituents of natural fibers are cellulose, hemicellulose, and lignin. Table 1 presents the composition of these constituents in untreated, alkali treated, and bleach treated switchgrass. Cellulose is capable of resisting strong alkali treatments, and its content remains relatively constant before and after treatments (Bismarck *et al.* 2005). For the alkali treated switchgrass, the cellulose content increased as the hemicellulose content decreased and the lignin content remained constant. As explained earlier, the hemicellulose component of natural fibers is soluble in alkaline solutions, whereas lignin is mainly affected by alkaline solutions at elevated temperatures. As such, the overall cellulose and lignin contents remained relatively the same. A comparison of the ratio of cellulose to hemicellulose revealed an increase from 1.54 to 4.6 from untreated to alkali-treated switchgrass. This indicates that upon alkali treatment, the cellulose content relative to the hemicellulose content was higher, signifying the removal of hemicellulose. Similarly, when comparing the cellulose to lignin content of untreated and alkali treated fibers, the ratio remained the same, indicating that the cellulose and lignin were unaffected by the alkali treatment.

Likewise, the addition of the bleaching components to an alkaline solution not only reduced the hemicellulose content, but also the lignin content. The bleach treatment clearly indicated a decrease in hemicellulose and lignin content. Similar results have been observed for alkali treated alfa stem fibers subjected to a bleach treatment using sodium hypochlorite (Borchani *et al.* 2015). Extreme reductions in hemicellulose and lignin contents have been observed by previous researchers. The contents were reduced from

30.2 to 3.7% hemicellulose content and from 19.9 to 0.8% lignin content in a 5% alkali solution (Borchani *et al.* 2015). It is usually not possible to completely remove the hemicellulose and lignin contents from lignocellulosic fibers through these types of treatments due to the hydrogen bonding that occurs between the remaining hemicellulose and cellulose fibrils and the chemically resistant bonds found in lignin (Saha *et al.* 2010).

Table 1. Compositional Analysis of Untreated and Treated Switchgrass

Switchgrass Sample	Cellulose (% dry matter)	Hemicellulose (% dry matter)	Lignin (% dry matter)	Cellulose: Hemicellulose	Cellulose: Lignin
Untreated	52.4±0.7	34.0±0.8	13±1	1.54±0.2	3.9±0.5
Alkali	70±2	15.3±0.8	14±1	4.6±0.4	5.0±0.6
Bleach	71.6±0.8	19±1	9.8±0.7	3.9±0.2	7.3±0.5

Thermogravimetric Analysis

The thermal stability of natural fibers is an important property to examine when considering their use in composite applications. Thermogravimetric analysis (TGA) was conducted on untreated and treated switchgrass. Figure 7 shows the TGA and derivative thermogravimetry (DTG). The constituents of natural fibers each have their own thermal stability, causing various degradation peaks observable in Fig. 7.

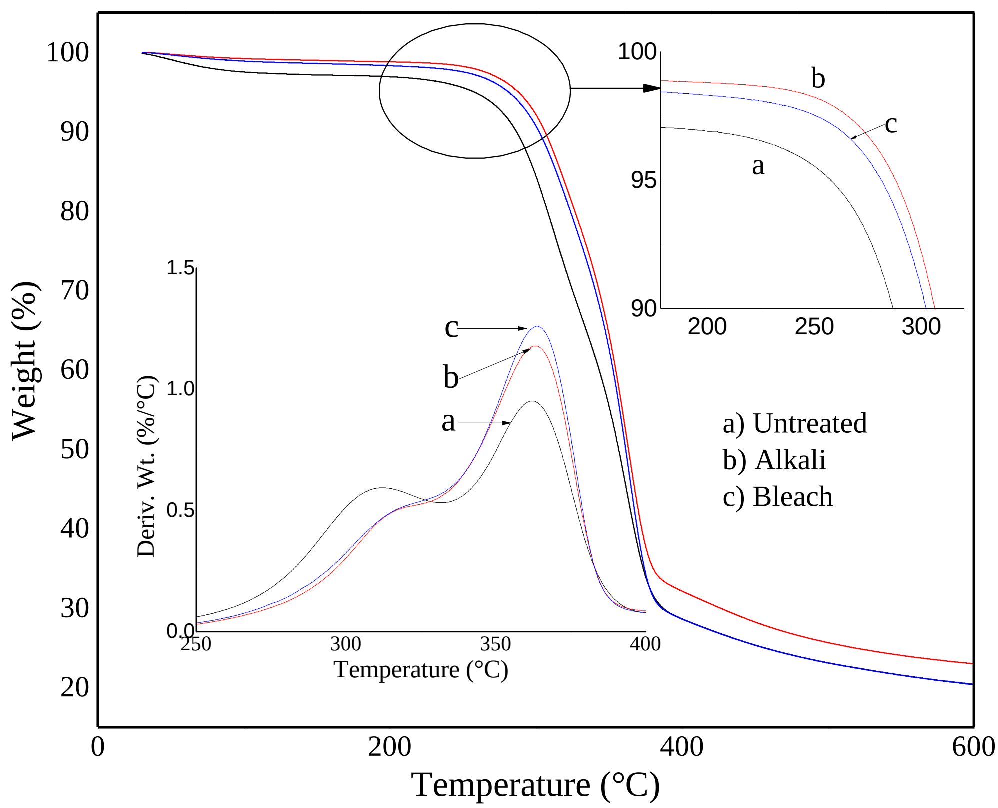

Fig. 7. TGA and DTG graphs of untreated and treated switchgrass

Switchgrass showed a 5 wt.% loss at 258 °C and exhibited two maximum degradation peaks at 312 and 362 °C, corresponding to hemicellulose and cellulose, respectively. The components of switchgrass have been found to have a maximum degradation temperature ranging from 286 to 295 °C for hemicellulose, 349 to 355 °C for cellulose, and 200 to 900 °C for lignin (Pasangulapati *et al.* 2012). The lignin component of natural fibers does not produce a definitive degradation peak because it has such a wide temperature range. However, since lignin begins to degrade at such a low temperature, it negatively affects the thermal stability.

Alkali and peroxide bleach treatments are capable of removing non-cellulosic components, which is beneficial for improving upon the thermal stability of natural fibers. By removing non-cellulosic components, the decomposition process relies more on the stability of cellulose. The temperature at 5 wt.% loss increased by 12 and 9% for alkali and bleach treatments, respectively. Along these lines, the maximum degradation peak of hemicellulose was reduced to a shoulder next to the maximum degradation peak of cellulose, which occurred at around 363 °C. The TGA results corroborate the fact that both treatments partially removed the hemicellulose content of switchgrass. However, it has been reported that a 5% concentration alkali solution was capable of completely removing hemicellulose, and partially removing other non-cellulosic components (Borchani *et al.* 2015).

Scanning Electron Microscopy

The surface morphology of untreated and treated switchgrass observed using scanning electron microscopy (SEM) is shown in Fig. 8. The surface of the untreated switchgrass is expected to contain more lignin, hemicellulose, and impurities such as pectin, and other non-cellulosic components. This is a common surface morphology for lignocellulosic fibers wherein cellulosic fibrils are bound together by cementing materials (Liu *et al.* 2004).

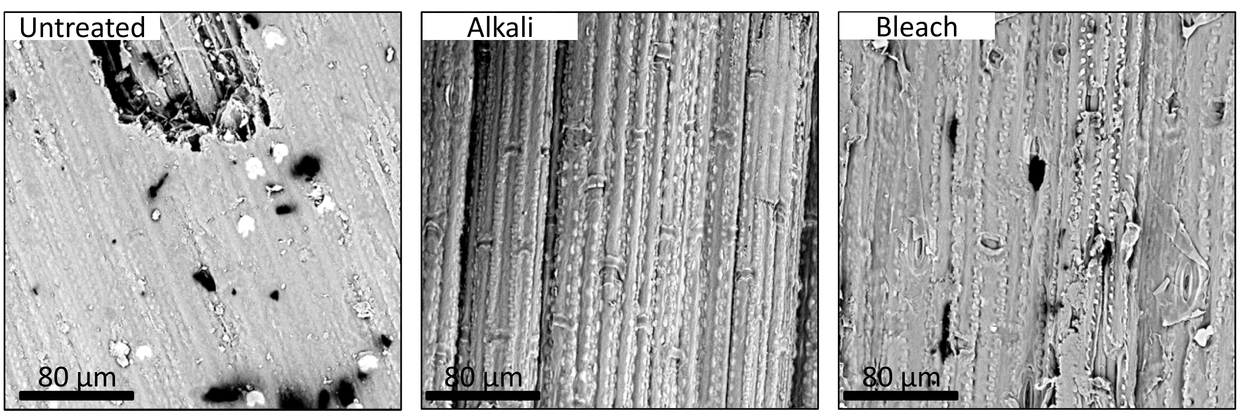

Fig. 8. SEM images of the surface morphologies of untreated and treated switchgrass

The alkali-treated switchgrass showed a surface that was much cleaner and relatively free from impurities, exposing the interlocked cellulose bundles. The structure of the switchgrass remained intact after alkali treatment since the majority, if not all, of the lignin was still present in the material and providing the structural integrity of the fiber. In contrast, the peroxide bleach treatment was capable of solubilizing and oxidizing the lignin found in switchgrass. Therefore, the structure of the switchgrass was affected, exposing more voids and cellulose fibrils. Both methods cleaned the surface impurities from the switchgrass while creating a rougher surface morphology. It is common for alkali-based treatments to clean and roughen the surface of the fibers, as can be seen for hemp (Mwaikambo and Ansell 2002), alfa (Borchani *et al.* 2015), century (Obi Reddy *et al.* 2013), and reed straw (Barman *et al.* 2014) fibers. The rougher surface caused by alkali and peroxide bleach treatments is expected to improve bonding between the fiber and the matrix through physical interlocking.

X-Ray Diffraction

X-ray diffraction (XRD) is often used to determine the crystallinity of natural fibers by highlighting the crystallographic planes found in the material. Common crystallographic planes found in natural fibers are (101), $(10\bar{1})$, (002), and (040) (El Oudiani *et al.* 2012). As can be seen in Fig. 9, three of the stated characteristic peaks can be found for untreated and treated switchgrass that correspond to the different lattice planes of the fiber.

The $(10\bar{1})$ crystallographic plane corresponds to the cellulose II structure, while the cellulose I structure correlates to the (002) plane. A transformation of cellulose I to cellulose II generally occurs after the treatment of natural fibers, which affects the cellulose structure by rearranging the order of the crystallites (Mwaikambo and Ansell 2002). Since the peak corresponding to the $(10\bar{1})$ plane was not apparent after the alkali or bleach treatments, the surface modification process was not harsh enough to affect the crystalline structure of cellulose and cause the transformation. Sodium hydroxide concentrations between 10 and 15% have been reportedly able to convert cellulose I structures to cellulose II (Borchani *et al.* 2015). This relates well to the reason why the peak for cellulose II was not evident following the studied alkali and bleach treatments, as their sodium hydroxide concentrations were not high enough.

Despite the lack of cellulose conversion, an increase in crystallinity index (CI) was observed after the two treatments. The CI of untreated switchgrass was calculated to be 29%. An increase to 43 and 40% for alkali and bleach treatments was observed, respectively. A higher crystallinity index was observed for the alkali-treated switchgrass compared to the bleach-treated switchgrass due to the higher alkali concentration. The sodium hydroxide concentration for the alkali-treated sample was 5%, whereas the bleach-treated sample was 3%. This resulted in higher removal of non-cellulosic materials. Liu *et al.* (2013) studied the effects of different sodium hydroxide concentrations on hemp fibers, wherein an increase of CI was observed up to a NaOH concentration of 10%, and then it subsequently dropped off.

Alkali-based treatments remove the amorphous fraction of the natural fibers, increasing the overall crystalline regions in the material, and therefore increasing the CI (Borchani *et al.* 2015). Consequently, with high alkali concentrations, the cell wall of the natural fiber will become damaged, reducing the crystallinity index and altering the configuration of cellulose (Liu *et al.* 2013).

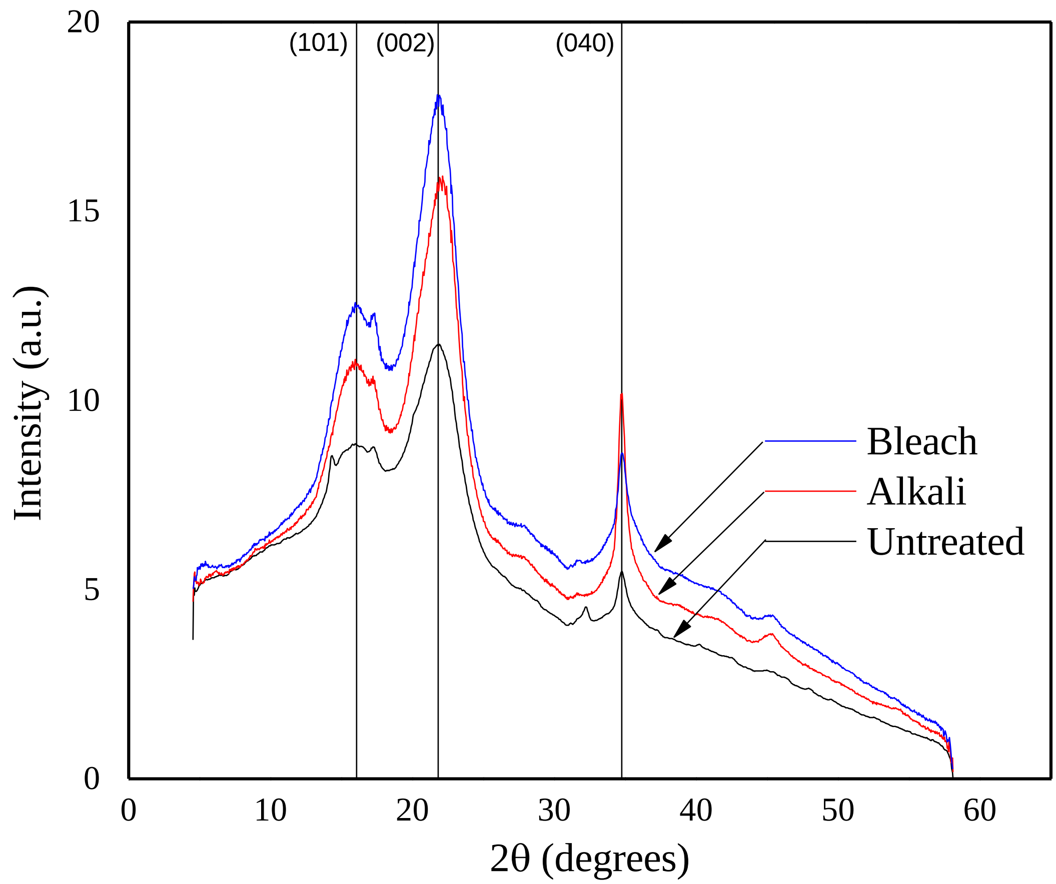

Fig. 9. XRD spectra of untreated and treated switchgrass

CONCLUSIONS

1. Alkali and bleach treatments modified the surface of switchgrass, affecting the chemical components and physical appearance of the fibers.
2. FTIR and compositional analysis showed evidence of the partial removal of hemicellulose and other surface impurities after alkali treatment, while lignin, hemicellulose, and other surface impurities were partially removed after peroxide bleach treatment.
3. TGA presented an increase in switchgrass thermal stability, where the onset degradation shifted to a higher temperature due to the removal of less stable compounds (hemicellulose, waxes, and other surface impurities).
4. SEM images of the alkali and bleach treated switchgrass showed a cleaner surface caused by the removal of non-cellulosic components, and a rougher surface morphology exposing the cellulose bundles and fibrils.
5. XRD analysis provided spectral information for calculating the crystallinity index of the switchgrass before and after treatments. An increase of the crystallinity index was observed after the alkali and bleach treatments compared to untreated switchgrass.

6. The use of surface treated switchgrass in composites would be beneficial due to an improved interfacial adhesion with the matrix caused by the increased surface roughness enhancing the mechanical interlocking of the matrix with the fiber.

ACKNOWLEDGEMENTS

The authors acknowledge the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA), the University of Guelph Bio-Economy-Industrial Uses Research Theme (Project # 200369), and the Natural Sciences and Engineering Research Council (NSERC) Canada - Discovery Grants (Project # 400322 and #401111) for their financial support in this research. The authors would like to thank Vidhya Nagarajan's insightful comments towards improving the quality of this paper.

REFERENCES CITED

Agilent Technologies (2013). "CrysAlis Pro," Version 1.171.36.28.

AOAC 973-18 (1977). "Fiber (acid detergent) and lignin (H_2SO_4) in animal feed," Association of Official Analytical Chemists International, http://www.aoacofficialmethod.org/index.php?main_page=product_info&cPath=1&products_id=1165,accessed on 14 Jul 2016.

AOAC 2002-04 (2005). "Amylase-treated neutral detergent fiber in feeds. Using refluxing in beakers or crucibles," Association of Official Analytical Chemists International, http://www.aoacofficialmethod.org/index.php?main_page=product_info&cPath=1&products_id=2851,accessed on 14 Jul 2016.

Barman, D. N., Haque, M. A., Kang, T. H., Kim, G. H., Kim, T. Y., Kim, M. K., and Yun, H. D. (2014). "Effect of mild alkali pretreatment on structural changes of reed (*Phragmites communis* Trinius) straw," *Environ. Technol.* 35(2), 232-241. DOI: 10.1080/09593330.2013.824009

Bismarck, A., Mishra, S., and Lampke, T. (2005). "Plant fibers as reinforcement green composites," In: *Natural Fibers, Biopolymers, and Biocomposites.*DOI: 10.1201/9780203508206.ch2

Borchani, K. E., Carrot, C., and Jaziri, M. (2015). "Untreated and alkali treated fibers from alfa stem: Effect of alkali treatment on structural, morphological and thermal features," *Cellulose* 22(3), 1577-1589. DOI: 10.1007/s10570-015-0583-5

Das, M., and Chakraborty, D. (2006). "Influence of alkali treatment on the fine structure and morphology of bamboo fibers," *J. Appl. Polym. Sci.* 102(5), 5050-5056. DOI: 10.1002/app.25105

Das, M., and Chakraborty, D. (2008). "Evaluation of improvement of physical and mechanical properties of bamboo fibers due to alkali treatment," *J. Appl. Polym. Sci.* 107(1), 522-527. DOI: 10.1002/app.26155

El Oudiani, A., Chaabouni, Y., Msahli, S., and Sakli, F. (2012). "Mercerization of *Agave americana* L. fibers," *J. Text. Inst.* 103(5), 565-574. DOI: 10.1080/00405000.2011.590010

Elenga, R. G., Djemia, P., Tingaud, D., Chauveau, T., Maniongui, J. G., and Dirras, G. (2013). "Effects of alkali treatment on the microstructure, composition, and properties of the *Raffia textilis* fiber," *BioResources* 8(2), 2934-2949. DOI: 10.15376/biores.8.2.2934-2949

Faruk, O., Bledzki, A. K., Fink, H. P., and Sain, M. (2012). "Biocomposites reinforced with natural fibers: 2000-2010," *Prog. Polym. Sci.* 37(11), 1552-1596. DOI: 10.1016/j.progpolymsci.2012.04.003

He, Z., and Ni, Y. (2008). "Peroxide bleaching of eucalyptus ctmp using magnesium hydroxide as the alkali source," *Appita Journal: Journal of the Technical Association of the Australian and New Zealand Pulp and Paper Industry* 61(6), 450-455, 460.

He, Z., and Wekesa, M. (2006). "Peroxide bleaching: A comparative study of $Mg(OH)_2$-based and NaOH-based peroxide bleaching of TMP: Anionic trash formation and its impact on filler retention," *Pulp Pap. Can.* 107(3), 29-32.

Imtiazuddin, S. M., and Tiki, S. (2015). "What is the jute fiber? Bleaching and dyeing processes of jute fiber," http://www.ptj.com.pk/Web-2014/12-2014/General-Article-AVM-Article.html. Accessed on 4 Jun 2015.

Indran, S., and Raj, R. E. (2015). "Characterization of new natural cellulosic fiber from *Cissus quadrangularis* stem," *Carbohydr. Polym.* 117, 392-399. DOI: 10.1016/j.carbpol.2014.09.072

Keshwani, D. R., and Cheng, J. J. (2009). "Switchgrass for bioethanol and other value-added applications: A review," *Bioresour. Technol.* 100(4), 1515-1523. DOI: 10.1016/j.biortech.2008.09.035

Khan, M. N., Bisoyi, D. K., and Shukla, J. (2012). "Comparative SAXS study of heated and alkali-treated sisal fibers," *J. Appl. Polym. Sci.* 125(3), 2356-2362. DOI: 10.1002/app.36460

Lange, H., Decina, S., and Crestini, C. (2013). "Oxidative upgrade of lignin - Recent routes reviewed," *Eur. Polym. J.* 49(6), 1151-1173. DOI: 10.1016/j.eurpolymj.2013.03.002

Li, J., Hu, H., Song, Y., and Chai, X.-S. (2015). "New evidence for the role of the borohydride pretreatment on the hydrogen peroxide bleaching of kraft pulp," *RSC Adv.* 5(119), 98067-98074. DOI: 10.1039/C5RA17964E

Li, X., Tabil, L. G., and Panigrahi, S. (2007). "Chemical treatments of natural fiber for use in natural fiber-reinforced composites: A review," *J. Polym. Environ.* 15(1), 25-33. DOI: 10.1007/s10924-006-0042-3

Li, Z., Court, G., Belliveau, R., Crowell, M., Murphy, R., Gibson, A., Wajer, M., Branch, B., and Ni, Y. (2005). "Using magnesium hydroxide ($Mg(OH)_2$) as the alkali source in peroxide bleaching at Irving paper," *Pulp Pap. Canada* 106(6), 24-28.

Liu, H., You, L., Jin, H., and Yu, W. (2013). "Influence of alkali treatment on the structure and properties of hemp fibers," *Fibers Polym.* 14(3), 389-395. DOI: 10.1007/s12221-013-0389-8

Liu, W., Mohanty, A. K., Drzal, L. T., Askel, P., and Misra, M. (2004). "Effects of alkali treatment on the structure, morphology and thermal properties of native grass fibers as reinforcements for polymer," *J. Mater. Sci.* 9(c), 1051-1054. DOI: 10.1023/B:JMSC.0000012942.83614.75

Liu, Y., and Hu, H. (2008). "X-ray diffraction study of bamboo fibers treated with NaOH," *Fibers Polym.* 9(6), 735-739. DOI: 10.1007/s12221-008-0115-0

Mohanty, A. K., Misra, M., and Drzal, L. T. (2001). "Surface modifications of natural fibers and performance of the resulting biocomposites: An overview," *Compos. Interfaces* 8(5), 313-343. DOI: 10.1163/156855401753255422

Mwaikambo, L. Y., and Ansell, M. P. (2002). "Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization," *J. Appl. Polym. Sci.* 84(12), 2222-2234. DOI: 10.1002/app.10460

Obi Reddy, K., Raja Narender Reddy, K., Zhang, J., Zhang, J., and Varada Rajulu, A. (2013). "Effect of alkali treatment on the properties of century fiber," *J. Nat. Fibers* 10(3), 282-296. DOI: 10.1080/15440478.2013.800812

Obi Reddy, K., Uma Maheswari, C., Shukla, M., Song, J. I., and Varada Rajulu, A. (2013). "Tensile and structural characterization of alkali treated borassus fruit fine fibers," *Compos. Part B Eng.* 44(1), 433-438. DOI: 10.1016/j.compositesb.2012.04.075

Ozturk, H. B., Potthast, A., Rosenau, T., Abu-Rous, M., MacNaughtan, B., Schuster, C. K., Mitchell, J. R., and Bechtold, T. (2009). "Changes in the intra- and inter-fibrillar structure of lyocell (TENCEL(R)) fibers caused by NaOH treatment," *Cellulose* 16(1), 37-52. DOI: 10.1007/s10570-008-9249-x

Pasangulapati, V., Kumar, A., Jones, C. L., and Huhnke, R. L. (2012). "Characterization of switchgrass, cellulose, hemicellulose and lignin for thermochemical conversions," *J. Biobased Mater. Bioenerg*y 6(3), 249-258. DOI: 10.1166/jbmb.2012.1216

Radiotis, T., Li, J., and Goel, K. (1999). "Fiber characteristics, pulpability, and bleachability of switchgrass," *TAPPI J.* 82(7), 100-106.

Rayung, M., Ibrahim, N. A., Zainuddin, N., Saad, W. Z., Razak, N. I. A., and Chieng, B. W. (2014). "The effect of fiber bleaching treatment on the properties of poly(lactic acid)/oil palm empty fruit bunch fiber composites," *Int. J. Mol. Sci.* 15(8), 14728-14742. DOI: 10.3390/ijms150814728

Razak, N. I. A., Ibrahim, N. A., Zainuddin, N., Rayung, M., and Saad, W. Z. (2014). "The influence of chemical surface modification of kenaf fiber using hydrogen peroxide on the mechanical properties of biodegradable kenaf fiber/poly(lactic acid) composites," *Molecules* 19(3), 2957-2968. DOI: 10.3390/molecules19032957

Ridzuan, M. J. M., Abdul Majid, M. S., Afendi, M., Aqmariah Kanafiah, S. N., Zahri, J. M., and Gibson, A. G. (2016). "Characterisation of natural cellulosic fibre from *Pennisetum purpureum* stem as potential reinforcement of polymer composites," *Mater. Des.* 839-847. DOI: 10.1016/j.matdes.2015.10.052

Saha, P., Manna, S., Chowdhury, S. R., Sen, R., Roy, D., and Adhikari, B. (2010). "Enhancement of tensile strength of lignocellulosic jute fibers by alkali-steam treatment," *Bioresour. Technol.* 101(9), 3182-3187. DOI: 10.1016/j.biortech.2009.12.010

Saheb, D. N., Jog, J. P., Nabi Saheb, D., and Jog, J. P. (1999). "Natural fiber polymer composites: A review," *Adv. Polym. Technol.* 18(4), 351-363. DOI: 10.1002/(SICI)1098-2329(199924)18

Salam, A., Reddy, N., and Yang, Y. (2007). "Bleaching of kenaf and cornhusk fibers," *Ind. Eng. Chem. Res.* 46(5), 1452-1458. DOI: 10.1021/ie061371c

Salam, M. A. (2006). "Effect of hydrogen peroxide bleaching onto sulfonated jute fiber," *J. Appl. Polym. Sci.* 99(6), 3603-3607. DOI: 10.1002/app.22954

Saravanakumar, S. S., Kumaravel, A., Nagarajan, T., and Moorthy, I. G. (2014). "Effect

of chemical treatments on physicochemical properties of *Prosopis juliflora* fibers," *Int. J. Polym. Anal. Charact.* 19(4), 383-390. DOI: 10.1080/1023666X.2014.902527
Segal, L., Creely, J. J., Martin, A. E., and Conrad, C. M. (1959). "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer," *Text. Res. J.* 29(10), 786-794. DOI: 10.1177/004051755902901003
Subramanian, K., Senthil Kumar, P., Jeyapal, P., and Venkatesh, N. (2005). "Characterization of ligno-cellulosic seed fibre from *Wrightia tinctoria*plant for textile applications - An exploratory investigation," *Eur. Polym. J.* 41(4), 853-861. DOI: 10.1016/j.eurpolymj.2004.10.037
Then, Y. Y., Ibrahim, N. A., Zainuddin, N., Chieng, B. W., Ariffin, H., and Yunus, W. M. Z. (2015). "Influence of alkaline-peroxide treatment of fiber on the mechanical properties of oil palm mesocarp fiber/poly(butylene succinate) biocomposite," *BioResources* 10(1), 1730-1746. DOI: 10.15376/biores.10.1.1730-1746
Xiang, Y. W. (1998). "Peroxide decomposition and its effect on bleaching of a TMP pulp," Master's Thesis, The University of New Brunswick, New Brunswick, Fredericton, Canada, http://www.nlc-bnc.ca/obj/s4/f2/dsk1/tape8/PQDD_0002/MQ46282.pdf Accesed on 17 Dec 2015.
Zhang, X., Wang, F., and Keer, L.M. (2015). "Influence of surface modification on the microstructure and thermo-mechanical properties of bamboo fibers," *Materials (Basel)* 8(10), 6597-6608. DOI: 10.3390/ma8105327

Article submitted: June 27, 2016; Peer review completed: August 7, 2016; Revised version received and accepted; August 15, 2016; Published: October 3, 2016.
DOI: 10.15376/biores.11.4.9922-9939