

CHLORINE DIOXIDE TREATMENT OF SISAL FIBRE: SURFACE LIGNIN AND ITS INFLUENCES ON FIBRE SURFACE CHARACTERISTICS AND INTERFACIAL BEHAVIOUR OF SISAL FIBRE/PHENOLIC RESIN COMPOSITES

Linxin Zhong, Shiyu Fu,* Feng Li, and Huaiyu Zhan

This paper describes an investigation of the influences of chlorine dioxide treatment on fibre surface lignin. The fibre surface characteristics and the interfacial behaviour of the sisal fibre/phenolic resin composites were also studied by SEM, AFM, and XPS. The results show that the surface of the untreated fibre contains a large amount of lignin with granular structure and non-granular structure. The surface lignin concentration is up to 51% for the untreated fibre, and then it decreases to 24% and 20% for fibres treated with 1.5 % and 2.0% chlorine dioxide, respectively. The removal of lignin from the fibre surface can enhance the interfacial strength of the composites, giving rise to increases by 36% and 28% in tensile strength and internal bonding strength. These results indicate that the surface properties of single sisal fibres can be tailored to improve the fibre/resin interface. Chlorine dioxide treatment has potential for surface modification of sisal fibre in engineering the interfacial behaviour of composites.

Keywords: Surface characteristics; Interface; Chlorine dioxide; Sisal fibre

Contact information: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China. *Corresponding author. Tel.: +8620-87112453; fax: +8620-22236078; E-mail address: shyfu@scut.edu.cn

INTRODUCTION

With the gradual depletion of petroleum resources in the last decade worldwide, fibres derived from plants are fundamentally important for the production of biocomposites, which have the advantages of renewability, biodegradability, abundance, low cost, and reduced health hazard, and thus have received considerable attention with the possibility of replacing synthetic fibres based on petrochemical sources.

Plant fibres are comprised of three major chemical components, namely cellulose, lignin, and hemicelluloses. The cellulose forms a skeletal frame that is surrounded and encrusted by the matrix substances (hemicelluloses and lignin) (Reddy and Yang 2005). Cellulose chains composed of glucose units are organized into the elementary fibril, which are arranged into microfibrils with a diameter of 10-50 nm in the presence of hemicelluloses and lignin (Paavilainen 2001). The microfibrils are subsequently aggregated into larger units called individual plant fibres with a diameter of 10-30 μm and further into fibre bundles with a diameter larger than 100 μm , (Oksman et al. 2009; Mathew et al. 2005). The elastic modulus of bulk natural fibres bundles is about 10 GPa; single cellulosic fibres separated from fibre bundles have an elastic modulus up to 40

GPa. On the other hand, microfibrils separated by hydrolysis followed by mechanical disintegration can show an elastic modulus of 70 GPa (Michell 1989). It was reported that the lateral strength of the single flax fibre was higher than that of flax fibre bundle and the axial tensile strength of single flax fibre approached the strength of glass fibre (van den Oever et al. 1999).

Unfortunately, cellulose material is mainly used in the form of fibre bundles in natural-fibre-reinforced composites due to their good dispersibility and the fact that complicated processes are not required (Hepworth et al. 2000). Recently, some researchers have investigated the properties of composites reinforced with single plant fibres, including wood pulp fibres (Gindl and Jeronimidis 2004; Awal et al. 2009), thermomechanical pulp fibre (Rials et al. 2001), and recycled fibre (Rials et al. 2001; Huda et al. 2006), due to the better mechanical properties and fewer flaws or weak links (e.g. due to lignin or hemicelluloses between fibres) (Andersons et al. 2005; Bullions et al. 2006; Lundquist et al. 2003). Higher aspect ratios, and proportion of cell wall contribute to the fibre/matrix interface (Oksman et al. 2009; Sbiai et al. 2008; Stuart et al. 2006; Le Guen and Newman 2007). These results indicate that single plant fibres will be a better alternative to conventional fibre bundles, and the surface properties of single plant fibres can be better engineered and will play a more important role in the interface of composites, mainly due to the much larger specific surface area (Keener et al. 2004; Mathew et al. 2005). However, few studies have focused on the influence of surface characteristics of single plant fibres on the interfaces within composites.

In the last decade, some studies have focused on the surface characteristics of single plant fibres from different pulping processes, chemical treatments, or biological treatments (Maximova et al. 2001; Koljonen et al. 2004; Simola et al. 2000; Koljonen et al. 2003; Kangas and Kleen 2004; Risén et al. 2004). It is evident that these treatments greatly affect the surface lignin of fibres and the final applications of fibres. However, there is little information available in literature about the influence of surface characteristics of single plant fibre on the interfacial behavior of composites. In the present work, we made an attempt to investigate the surface characteristics of individual sisal fibres and their influence on the interfacial behaviour of sisal fibre/phenolic resin composites mainly by characterizing the surface lignin of the single sisal fibre. Chlorine dioxide treatment had been used as a lignin modification to enhance the interfacial adhesion between fibre bundle and phenolic resin, while the cellulosic part was preserved (Hoareau et al. 2004; Trindade et al. 2004, 2005; Hoareau et al. 2006; Megiatto et al. 2007). On the other hand, the selective oxidation of lignin induced by chlorine dioxide also was found to cause a serious degradation of lignin units (Megiatto et al. 2007). This degradation is extremely important for the chlorine dioxide bleaching of pulp fibre in the paper-making industry, of which the main object is to remove as much lignin as practical (Brogdon et al. 2005; Svenson et al. 2005, 2006). In this study, we adopted chlorine dioxide to selectively remove lignin from the fibre surface. The surface characteristics of single sisal fibres and the interfacial behaviour of the ensuing composites were investigated by SEM, AFM, and XPS. Such understanding will help better design the surface of single sisal fibre, and thus improve the plant fibre/resin interface.

EXPERIMENTAL

Materials

Sisal fibre bundle and phenolic resin (5123, free phenol \leq 1.5%, gel time 70~80s at 150 °C) were obtained from Dongfang Sisal Group CO., LTD and Haiyan Huaqiang Resin CO., LTD, respectively.

Preparation of Sisal Single Fibre

An ordinary soda pulping process (NaOH and anthraquinone) was used to break the bonds of lignin to separate sisal fibre bundles into single fibre (Rosli et al. 2003; Khristova et al. 2002). Fibre bundle (200 g) was pulped with a liquor-to-fibre ratio of 4:1 by weight, a NaOH charge of 18%, and an anthraquinone charge of 0.05% of the oven-dried weight of fibres. The temperature was raised from ambient to 165 °C over 60 min and held for a cooking time of 150 min in a high pressure reactor. The pulp fibre was washed with water until the pH of the filtrate was approximately 7.0, and then kept wet in plastic bags until required.

Treatment of Chlorine Dioxide

Delignification of fibers was performed with chlorine dioxide/water solutions (0.5%, 1.0%, 1.5%, and 2.0% of the oven-dried weight of fibres) at 10% consistency (by mass), pH 4 (adjusted with sulfuric acid), and 75 °C for 60 min. Thereafter, the fibre was washed with distilled water until the pH of the filtrate was approximately 7.0, and then kept wet in plastic bag until required.

Lignin content of fibre was measured with the kappa number method according to the TAPPI standard (T236). The kappa number is defined as the amount (milliliters) of a 0.1 N KMnO₄ solution consumed by 1 g of moisture-free pulp under standard conditions (Paice et al. 1993).

Surface Analysis by SEM

Scanning electron microscopy images were obtained using an SF-3700 microscope (Hitachi Co. Ltd.), operated in secondary electron mode at a beam current of 100 mA and an accelerating voltage of 10 kV. Samples were previously coated with gold for 150 s.

Surface Analysis by AFM

Atomic force microscopy (AFM) micro-nano morphology of fibre surfaces was studied by atomic force microscopy (AFM) using a Nanoscope III (Veeco Co. Ltd.) system equipped with a “vertical engage” J-scanner operating in tapping mode in air. Samples for AFM were prepared by dropping well-dispersed fibre suspensions onto a mica surface and then air drying at ambient temperature. AFM scanning was conducted at two to four locations on each fibre, and three different fibres were analyzed. All the images were recorded in the tapping mode using silicon cantilevers with a resonance frequency between 250 and 300 kHz and scan angle of 0°. The scan rate was 1 Hz.

Tapping force was controlled by the ratio between setpoint amplitude (A_{sp}) and free-air amplitude (A_0). A light tapping force ($A_{sp}/A_0 = 0.7-0.8$) was applied. Amplitude images were recorded, since they provide a map of the slope of the sample and ably display its shape and surface features.

Surface Analysis by XPS

In x-ray photoelectron spectroscopy (XPS) analysis, pulp sisal fibres (SFs) were first formed into small sheets (diameter: 20mm, basis weight: 80 g/m²) by using a screen filter (200 mesh), and thereafter dried at room temperature before extraction and XPS measurements. Then the sheets were placed in a flask and refluxed for a period of 4 h using 150 mL of acetone at 80 °C, and then oven dried at 50 °C for 6 h. XPS spectra of fibre handsheet surfaces were obtained with a XPS instrument (Axis Ultra DLD, Kratos Co.) equipped with a monochromatic Al K α X-ray source, operated at 150 W and with an electron flood gun for charge compensation. The analyzed area was 700 $\mu\text{m} \times 300 \mu\text{m}$ of fibre handsheet surface. The pass energy was 160 eV and 40 eV for low and high resolution, respectively. The relative amount of O/C ratio was determined from low-resolution XPS spectra, and the relative amounts of different bound carbons were determined from high-resolution C1s spectra (Dorris and Gray 1978a, 1978b). The chemical shifts relative to C–C (C1, 284.6 eV) for C–O (C2), O–C–O, or C=O (C3), and O=C–O (C4) were 1.7 ± 0.1 , 3.1 ± 0.1 , and 4.4 ± 0.2 eV, respectively. Surface coverage of lignin was determined using the C1 peak for the acetone-extracted samples, and surface extractives of the raw fibre were determined by the extracted and unextracted samples.

Preparation of Composites

Sisal fibers were dispersed in water and stirred for 5min. Then the water suspension was vacuum filtered using a screen filter (200 mesh) to form a fibre mat (about 1.00 mm thick), which was oven dried at 90 °C for 5 min, and then the fibre mat was immersed in phenolic resin (diluted in ethanol and in the presence of hexamine of 8%) for 10 min. The resin-impregnated mat was taken out and dried at 60 °C to remove ethanol, and then the fibre mat was pressed at 180 °C for 5 min under the pressure of 5 MPa. Finally, the fibre mats were dried at 160 °C for 1 h to get the composites. The dosage of phenolic resin was not varied (30%) in all composites.

Mechanical Properties of Fibre and Composites

Tensile stress-strain measurements were carried out using an Instron Universal Testing Machine 5565 with a load cell of 2000 N. Experiments were performed with a cross head speed of 10 mm/min at room temperature (25 °C) for tensile testing.

The internal bonding strength was measured according to the Scott bond strength method in an internal bonding testing machine (TMI 80-01-01-0002). The principle behind the method is to measure the strength needed to tear the metal blocks apart (z-directional tensile strength) and tear the metal gauge off the composite sample by delaminating the composite.

RESULTS AND DISCUSSION

Kappa Number of Fiber

The reactions of chlorine dioxide with lignin include phenolic structure and non-phenolic structure of lignin units, resulting in lignin degradation (Brogdon et al. 2005; Svenson et al. 2005, 2006). **Table 1** shows the kappa numbers of the fibres with and without chlorine dioxide treatment. The kappa number decreased dramatically from 10.3 for the sample without treatment to 7.9 for the sample treated with 0.5% chlorine dioxide, and then it decreased slowly to 6.5, 5.8, and 5.3 for the fibres treated with 1.0%, 1.5% and 2.0% chlorine dioxide, respectively.

Table 1. The Kappa Numbers of Fibres

Dosage of ClO ₂ (%) ^a	0	0.5	1.0	1.5	2.0
Kappa number	10.3	7.9	6.5	5.8	5.3

^a The dosage of ClO₂ based on oven dried fibers.

SEM Analysis of Fibre Surface

Soda pulping is a process to separate fiber bundles into single fibres by primarily dissolving and removing lignin and hemicelluloses among fibres in alkaline solutions at high temperature and pressure. The morphology of the single fibre is shown in Fig. 1a.

The single fibre was observed to be irregular, exhibiting an inhomogenous surface that was covered by a thin layer of non-cellulose material, exposing a wrinkled surface (Fig. 1a). Since the fibre cell wall consists of microfibril aggregates embedded in a matrix of lignin and hemicelluloses, the non-cellulose material mainly corresponds to lignin (Lindström 1979; Sundin and Hartlier 1998). During pulping processes, the dissolved lignin would precipitate on the fibre surface again at the final stage of pulping, washing, and bleaching, forming a lignin-concentrated surface (Maximova et al. 2001; Koljonen et al. 2004). The irregular shapes are supposed to produce a larger contact area and stronger mechanical interlocking strength between fibre and resin. For the fibre treated with chlorine dioxide, the wrinkled surface was more visible, forming a rougher surface, especially for the samples treated with 1.5% and 2.0% chlorine dioxide (Fig. 1c and Fig. 1d). These observations indicate that chlorine dioxide treatment can efficiently remove the residual lignin from the fibre surface.

AFM Analysis of Fibre Surface

AFM has a much better resolution, allowing the fibre surface to be observed on a nanometre scale, and thus provides more details about fibre surface characteristics. Figure 2a-c features the surfaces of the fibres with and without chlorine dioxide treatment. The surface of the untreated sisal fibre was covered with a thin layer material with granular structure, resulting in less exposure of microfibrils (Fig. 2a). Similar observations have also been reported in previous works (Simola et al. 2000; Koljonen et al. 2003; Kangas and Kleen 2004). Simola et al. (2000) pointed out that the particles on

pulp fibre surface corresponded to lignin, because the decrease in the relative amount of the granular phase correlated well to a decreasing kappa value of pulp fibre. Koljonen et al. (2003) and Kangas and Kleen (2004) also reported that the surfaces of unbleached mechanical pulp fibres consisted of large amount of granular lignin. These granular materials can mainly correspond to the precipitated lignin during pulping, washing, or treatment processes (Lindström 1979; Sundin and Hartlier 1998; Maximova et al. 2001; Koljonen et al. 2004). Therefore, the coverage of the precipitated lignin results in a lignin-concentrated surface (Fig. 2a) and the relatively smooth surface in SEM image (Fig. 1a).

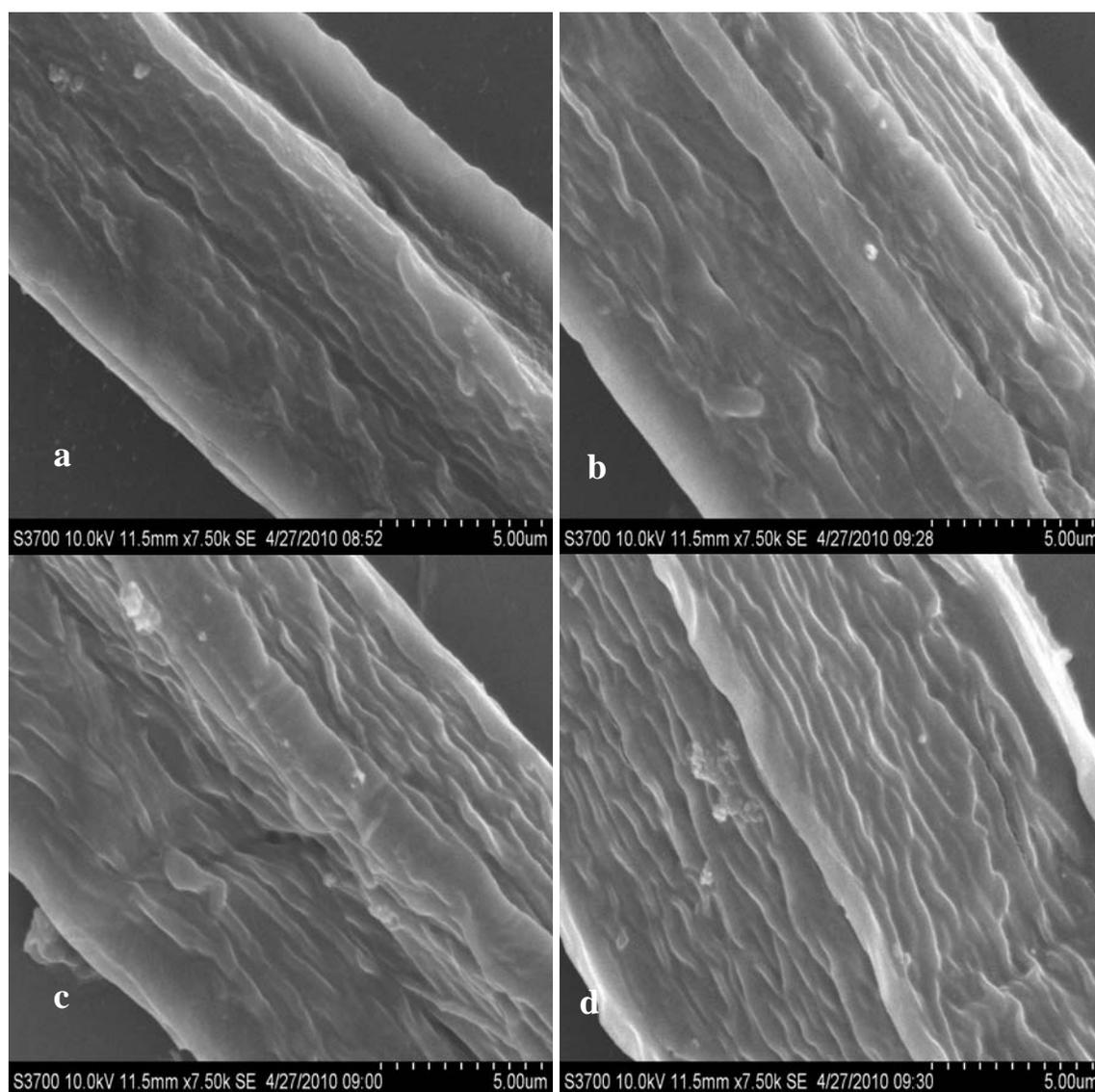


Fig. 1. The SEM morphologies of fibres: (a), (b), (c), and (d) represent the samples treated with chlorine dioxide of 0%, 1.0%, 1.5%, and 2.0%, respectively.

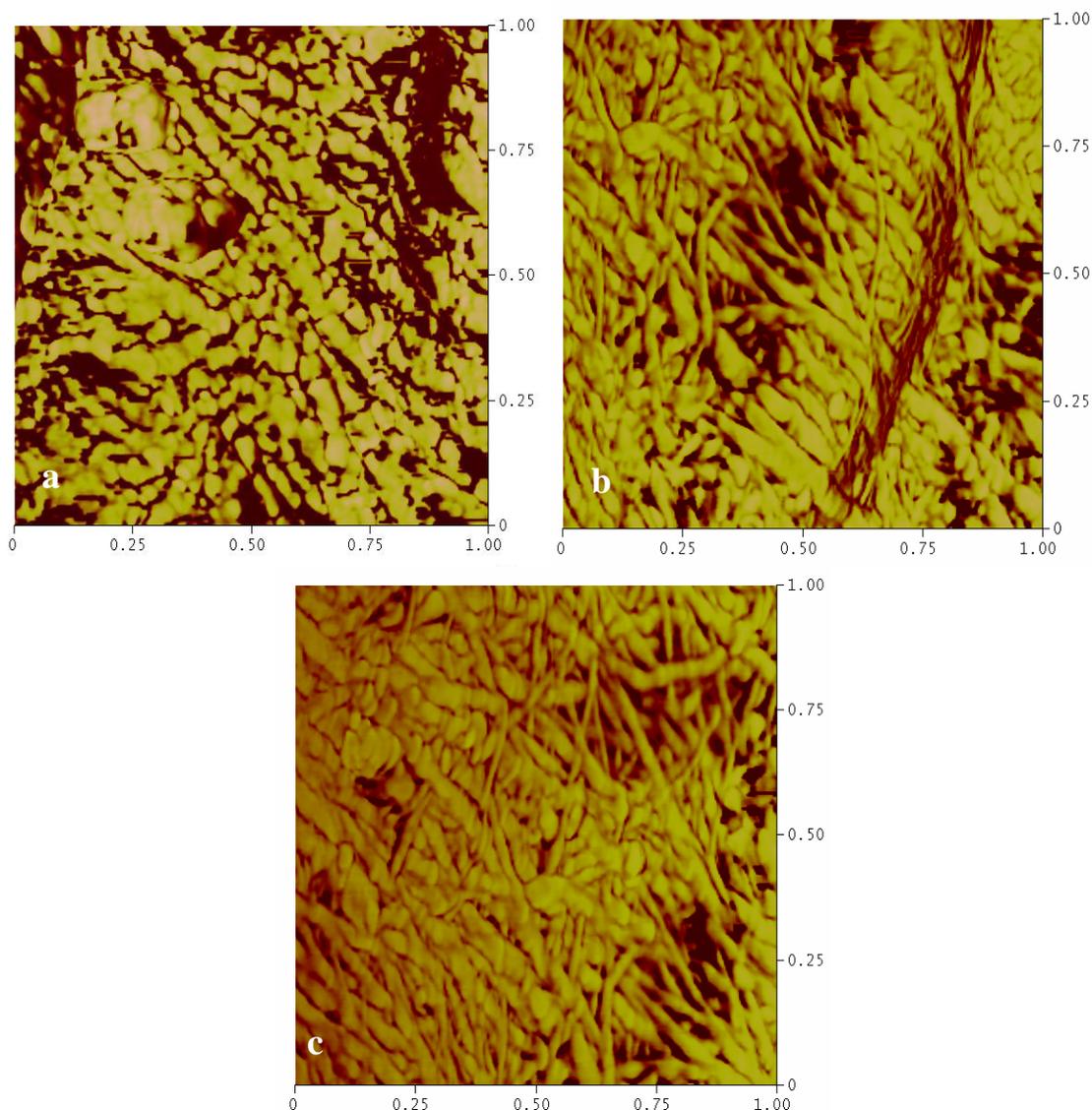


Fig. 2. AFM micrographs of SF surfaces: (a), (b), and (c) represent the fibres treated with chlorine dioxide of 0%, 1.5%, and 2.0%, respectively.

In the case of the fibres treated with chlorine dioxide (Fig. 2b-c), both the amount and size of the surface lignin decreased, and the poorly-oriented cellulose microfibrils with a diameter of 20-50 nm can be clearly observed on fibre surface, featuring the primary layer of fibre cell wall (Fujita and Harada 1991). These observations evidently indicate that the surface lignin was significantly removed by chlorine dioxide treatment, leading to the more exposure of the real fibre surface with poorly-orientated cellulose microfibrils and a rougher surface (Fig. 1b-d). Similar results were also reported when pulp fibres were subjected to bleaching agents (Koljonen et al. 2003).

XPS Analysis of Fibre Surface

The standard testing methods for lignin content, such as Klason lignin analysis and determination of kappa numbers, are routinely used in evaluations of fibre bulk lignin (Sjöström 1993). However, the distribution of surface lignin closely related to interfacial behavior cannot be characterized by these methods. X-ray photoelectron spectroscopy (XPS) has been shown to be a useful tool in analyzing the chemical composition of fiber surfaces. The core of the XPS method for fibre surface research lies in oxygen and carbon analyses. The lignin concentration on the fibre surface can be obtained by the atomic oxygen to carbon ratios or the amount of C1. In the cases of cellulose, hemicelluloses, lignin, and extractives, carbon and oxygen are the only elements available, since hydrogen cannot be detected by XPS. Only a layer about 10 nm thick of sample surface is detected by XPS. In the present work, XPS was used to investigate the influence of chlorine dioxide treatment on fibre surface characteristics.

The theoretical O/C ratios of cellulose and lignin are 0.83 and 0.33, respectively. Higher O/C ratio indicates lower lignin concentration (Dorris and Gray 1978a, 1978b). Therefore, surface lignin concentration can be interpreted by the O/C ratio in low resolution XPS spectra. On the other hand, a high resolution carbon spectrum can be deconvoluted into different carbon components, i.e., carbon with different chemical environments according to Dorris and Gray (1978a,b). The types of chemical bonds of carbon in cellulose, hemicelluloses, lignin, and extractives can be categorized into four groups: C1 (C-C, C-H, C=C), C2 (C-O or C-O-C), C3 (C=O or O-C-O), and C4 (O-C=O). C1 exists in lignin and extractives, and can only refer to lignin when the extractives are removed by acetone, but not in cellulose and hemicelluloses. On the other hand, C2 and C3 are considered to refer to cellulose and hemicelluloses, and C4 exists in carboxylic acids. Therefore, by determining the percentage of C1, the surface lignin and extractives concentration can be compared. Quantification of the surface lignin and extractives is based on C1 percentages, as shown by Eq. (1) and Eq. (2), respectively (Koljonen et al. 2003). In equation (1), the value 49% represents the amount of C1 in pure milled wood lignin and X is the level of contamination (2%) (Koljonen et al. 2003). Results obtained by XPS are shown in Fig. 3 and Table 2.

$$\phi_{lignin} = \frac{C1_{extracted} - X}{49\%} \times 100\% \quad (1)$$

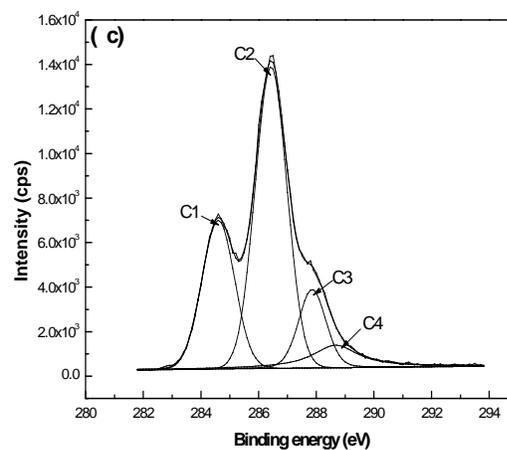
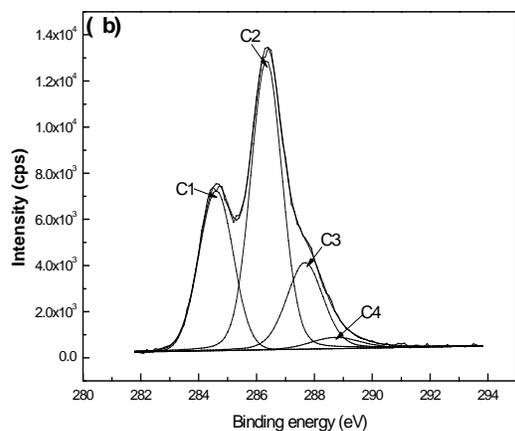
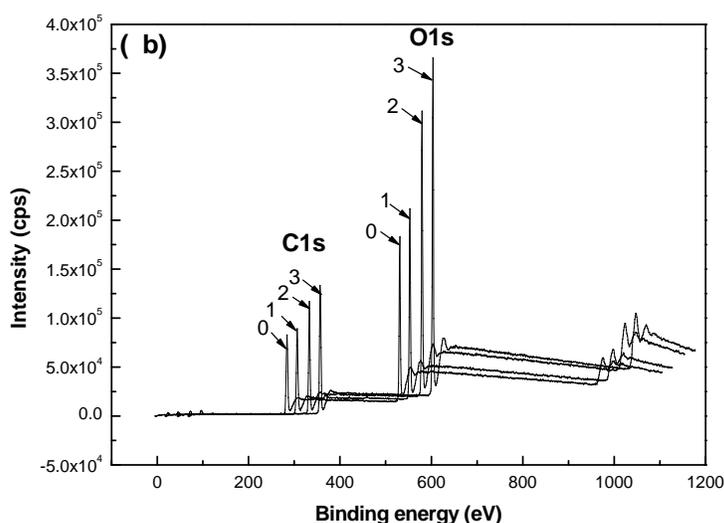
$$\phi_{extractes} = (C1_{unextracted} - C1_{extracted}) \times 100\% \quad (2)$$

Although the kappa number of the fibre treated with 2.0% chlorine dioxide decreased to a relatively low value, the results obtained from XPS still show a surface with up to 20% lignin. The residual lignin mainly was present in the form of particles, which can be identified in Fig. 2d. Koljonen et al. (2003) found that the thermo-mechanical pulp fibre had a surface lignin content of more than 20% after ozone treatment. Risén et al. (2004) also reported that although oxygen delignification decreased the surface lignin by about 39%, the residual surface lignin was still up to 10%. The precipitation of lignin during treatment and the low chemical reactivity of the residual lignin due to condensed structures and lignin-carbohydrate complexes can be proposed as reasons for this relatively high-lignin surface (Koljonen et al. 2003).

Table 2. XPS Data of the Extracted Sisal Fibres

Samples	Atomic ratio (O/C)	C1s total= 100%				ϕ_{lignin} (%)	$\phi_{extractives}$ (%)
		C1 (%)	C2 (%)	C3 (%)	C4 (%)		
0	0.43	29	50	18	3	50	2*
1	0.47	27	52	12	9	51	—
2	0.54	14	62	16	3	24	—
3	0.59	12	62	23	3	20	—

Note: 0 and 1 represent the raw fibres before and after acetone extraction, while 2 and 3 represent the fibres treated with chlorine dioxide at the 1.5% and 2.0% levels, respectively. The table shows atomic ratios of O/C in low-resolution survey scans and the amount of C1 in high-resolution carbon spectra (carbon in different functional groups with oxygen). * Extractives can be only detected in the sample without extraction, because the extractives were removed from the sample by acetone.



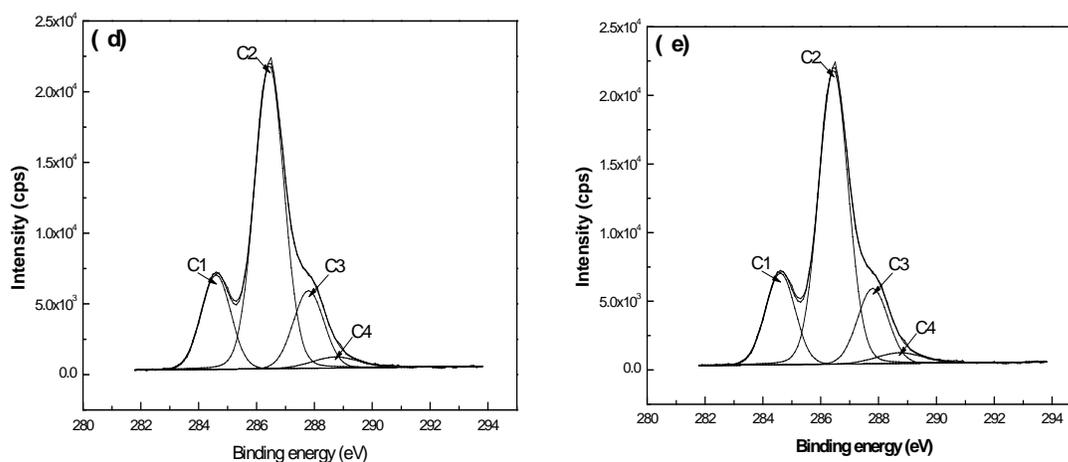


Fig. 3. XPS spectra of the sisal fibres: (a) low-resolution survey scans of O1s and C1s, (b)-(e) high-resolution spectrums of the C1s for the raw fibre, extracted raw fibre and the fibre treated with 1.5% and 2.0% chlorine dioxide, respectively.

Tensile Properties of Composites

The tensile strengths of the composites are shown in Fig. 4 and Table 3. The tensile stresses at break were 22.7 MPa, 26.8 MPa, 29.7 MPa, 30.2 MPa, and 30.8 MPa for the composites obtained with the untreated fibre, fibres treated with 0.5%, 1.0%, 1.5%, and 2.0% chlorine dioxide, respectively, representing increases by 18%, 30%, 33%, and 36%, indicating substantial improvement in the fibre/resin interfacial adhesion.

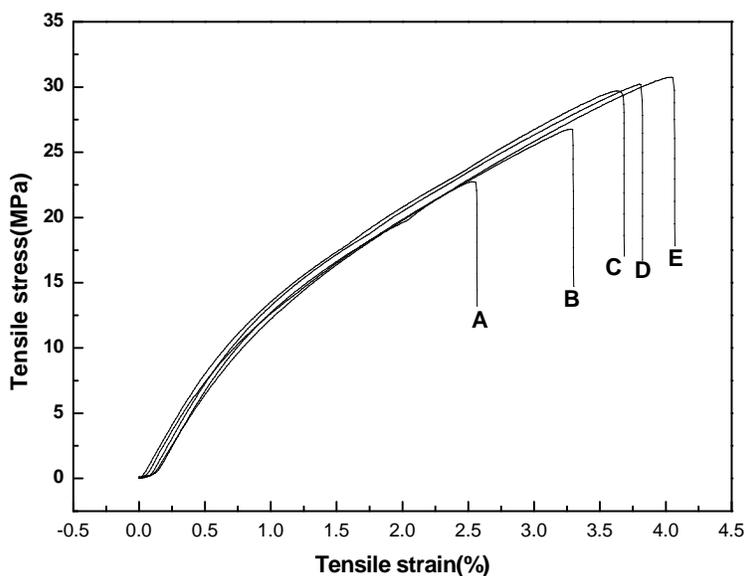


Fig. 4. Effect of chlorine dioxide treatment on the tensile strength of composites. The samples A, B, C, D, and E represent the composites obtained with the untreated fibre, and fibre treated with 0.5%, 1.0%, 1.5% and 2.0% chlorine dioxide, respectively.

Table 3. Tensile Stresses and Strains of the Composites

Samples	A	B	C	D	E
Stress (MPa)	22.7	26.8	29.7	30.2	30.8
Strain (%)	2.5	3.3	3.6	3.8	4.0

SEM micrographs of fibres (Fig. 1) show that the decrease in surface lignin can increase the surface roughness and specific surface area, which results in larger contact area between fiber and resin, and thus producing a stronger mechanical interlocking strength (Le Guen and Newman 2007; Bisanda 2000). Bledzki et al. (2004) pointed out that the rough fibre surface resulting from maceration furthered the wettability and form fit of the matrix material, thus caused a better fiber/matrix adhesion. Furthermore, the chemical reaction between plant fibre and phenolic resin mainly involves the methylol and phenolic hydroxyl groups of resin with cellulosic hydroxyl groups (Sreekala et al. 2000). The removal of lignin from the fibre surface allows more exposed hydroxyl groups, because cellulose can provide more hydroxyl groups and thus facilitate the chemical reaction between plant fibre and phenolic resin, resulting in stress transferring more efficiently at the interface.

Finally, the interface between fibre and resin may involve cellulose microfibrils, lignin, and phenolic resin in the presence of surface lignin, contributing to the strength of adhesion at the microfibril/lignin interface, lignin/resin interface, and microfibril/resin interface accordingly. Among these three kinds of interfaces, the microfibril/surface lignin interface is supposed to be the weakest interface because most of the surface lignin results from the dissolved lignin precipitating on fibre surfaces rather than the original lignin embedded into microfibrils skeleton (Maximova et al. 2001; Koljonen et al. 2004), forming a relatively weak interfacial adhesion between surface lignin and surface microfibril of cell wall. This weak interface may be the source of cracks that lead to composites fracturing when load transfers through the interface. When more surface lignin is removed, the weak interface between surface lignin and microfibril will be less, and larger amounts of phenolic resin can contact with microfibrils directly, resulting in a stronger interface with fewer cracks.

The surface of untreated fibre was relatively smooth and covered by blurry microfibrils (Fig. 1a). However, the fracture surface of the fibre in Fig. 5a shows a clear wrinkled area after fracturing, which can be taken as an indicator of a weak interface between fibre and resin due to the surface lignin disfavoring the fibre/resin interaction or the weak microfibril/surface lignin interface. In this case, cracks easily developed and thus load could not be efficiently transferred, resulting in resin becoming disconnected from the fibre surface. The failure surface of the treated fibre, however, showed a significant difference from that of untreated fibre, as shown in Fig. 5b. The wrinkled fibre surface as shown in Fig. 1c, became blurry due to the presence of resin, which indicates stronger interface strength between resin and the outer cell wall. In this case, the removal of surface lignin gave rise to stronger physical and chemical interaction between plant fibre and phenolic resin, as well as stronger adhesion at the interface, resulting in stronger interfacial strength and tensile strength.

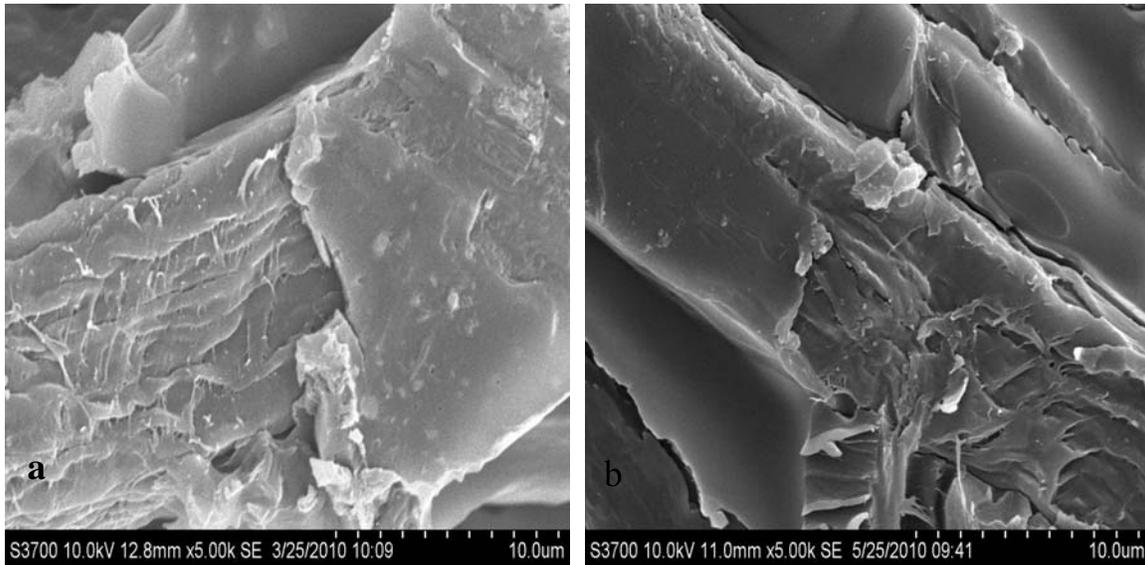


Fig. 5. SEM micrographs of tensile failures of fibres: (a) untreated fibre and (b) fibre treated with 1.5% chlorine dioxide

Internal Bonding Strength of Composites

The internal bonding strength can be defined as the strength in the z-direction, such as at a 90° angle to the plane of the fibre mat composites, and is more dependent on the interfacial strength rather than on fibre mechanical properties. It was found that the internal bonding strength also benefited from the treatment of chlorine dioxide (Fig. 6), increasing by increments of 12%, 22%, 26%, and 28% for the fibre treated with 0.5%, 1.0%, 1.5%, and 2.0% chlorine dioxide, respectively, indicating significant improvement in the interfacial adhesion between fibre and resin.

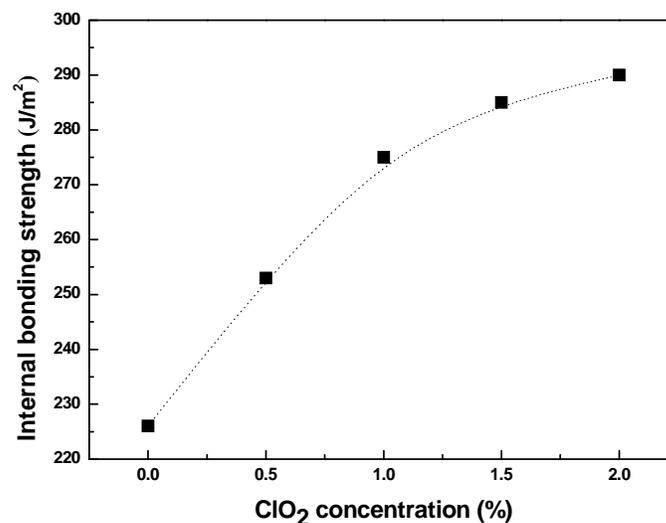


Fig. 6. Effect of chlorine dioxide treatment on the internal bonding strength of the composites

These results again confirm that the interfacial strength benefited from the removal of surface lignin. In addition, the cellulose-rich fibre surface would further facilitate chemical modifications to obtain better interfacial strength, for example, by means of acetylation, silane treatment, TDIC treatment, acrylation, and acrylonitrile grafting, all of which are dependent on the presence of –OH groups provided by cellulose microfibrils on the fibre surface (Sreekala et al. 2000; Mathew et al. 2005; Das and Chakraborty 2009).

CONCLUSIONS

1. Surface lignin plays an essential role in the surface characteristics of fibre and the interfacial behaviour of composites prepared with cellulosic materials. The sisal fibre surface is covered with large amounts of lignin, and relatively few cellulose microfibrils are exposed. These conditions do not favor effective bonding at the fibre/resin interface.
2. The significant removal of lignin from the fibre surface can be achieved by chlorine dioxide treatment, thus promoting the fibre/resin interface by increasing the interlocking strength, chemical bonding strength between fibre and resin, and eliminating the weak interface.
3. These results indicate that the interface of cellulose-reinforced composites can be better enhanced by engineering the surface properties of single fibres. Chlorine dioxide treatment can be a potential alternative to modify plant fibre surface and the interfacial behaviour of composites.

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