Surface Characterization of Plasma-treated Eucalyptus Alkaline Peroxide Mechanical Pulp using Electronic Spectroscopy Chemical Analysis and Atomic Force Microscopy

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Eucalyptus alkaline peroxide mechanical pulp (APMP) fibers were modified by a low-temperature plasma (LTP) treatment within an air and oxygen mixture. An atomic force microscope (AFM) and electronic spectroscopy chemical analysis (ESCA) were used to analyze the morphological and chemical information of eucalyptus APMP fibers. According to the AFM results, LTP treatment etched the fibers' surface, allowing for the removal of hydrophobic substances from the surface. According to the ESCA, the oxygen to carbon ratio of the APMP fiber surface increased from 50.08% to 55.47%, and the C1 peak area decreased from 8.89% to 8.45% after a LTP treatment. All of these results indicate that a LTP treatment can modify the APMP fibers and reduce the contents of lignin and extractives, thus exposing more carbohydrate.

Keywords: Low-temperature plasma; Eucalyptus APMP; ESCA; AFM

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INTRODUCTION

Lignin and extractives are not evenly distributed in wood fibers because of their heterogeneous structure and the different processing methods used during defibration and washing. Since the hydrophobic substances on the fibers' surfaces have a major influence on the strength properties of mechanical pulps, analyzing and researching the surface chemical properties of fibers will prove very useful.

Alkaline peroxide mechanical pulp (APMP) may have many advantages, including high yield and low pollution, but the lignin content on the APMP fiber surface remains high. A rigid intercellular layer covers the fiber surface, which results in poor flexibility in the APMP fibers and also seriously affects the binding strength between the fibers. The large hydrophobic areas on the surface of the mechanical pulp fiber reduce the wettability and impair the absorption properties. With the reduced absorbency of mechanical pulps, their use has been limited in the papermaking industry. In order to solve these issues, many different ways have been developed to improve the physical properties of APMP fibers simply by modifying the fibers. After modification, the application of APMP fibers can be extended.

Low-temperature plasma (LTP) treatment is a well-known fiber modification technology that features low energy consumption, environmentally friendly character, and minimization of damage to the fibers. It is easy to control the area and the degree of modification, while using low-temperature plasma treatment to modify the fibers. When

the activated species within the low-temperature plasma strike on the materials' surface, new free radicals form on the surface of the material. These free radicals greatly change the property of the material's surface.

Earlier studies by Carlsson, Gilbert *et al.* (1994) and Carlsson, Ströem *et al.* (1995) have shown that low-pressure cold plasma of O_2, N_2, Ar, or air can be employed to improve the water sorption of chemical and mechanical pulps. An oxygen plasma can be expected to increase the hydrophilic nature of cellulosic surfaces (Vesel and Mozetic 2009). Alternatively, the high-energy species generated during plasma treatment of a surface can be utilized to initiate free-radical polymerization of organic molecules and corresponding grafting reaction on a cellulosic surface (Alf *et al.* 2010). Flynn *et al.* (2013) report changes to surface properties of cellulose by a dielectric barrier discharge (DBD) plasma operating at atmospheric pressure in both air and an ammonia/nitrogen gas mixture and found that the water contact angle for cellulose processed in air decreased and increased in surface roughness significantly after exposure to DBD. Lekobou *et al.* (2016) used atmospheric pressure weakly ionized plasmas with argon and acetylene to deposit plasma-polymerized coatings on wood veneers (birch, maple), cellulose paper, and pine wood flour to modify their surface properties, in particular their topography and wettability. The treatment can change their wettability from hydrophilic to hydrophobic. Wu *et al.* (2008) found the surface of cellulose treated by the argon DBD plasma was significantly etched, and the relevant force of hydrogen bonding was decreased, together with the solubility improvement of natural cellulose in the diluted alkaline solution. In addition, bleached softwood kraft and unbleached softwood thermomechanical pulp handsheets were modified under low-temperature plasma treatment and the physical properties of the paper were enhanced greatly according to Vander Wielen *et al.* (2005). Zanini *et al.* (2005) modified the structure of the lignocellulosic fibers by using cold argon (Ar) plasma treatments. The research showed that the plasma treatment can greatly modify the chemical structure of lignin. The treatment decreased the number of phenoxy groups in both chemi-thermo-mechanical pulp (CTMP) and kraft fibers, and then regenerated new structures, such that the content of lignin on the surface was greatly reduced.

Two different approaches to determining pulp fiber surface properties have appeared in recent years. One approach uses an atomic force microscope (AFM), which can be used in the study of surface morphology. The other approach consists of spectroscopic methods, such as electron spectroscopy for chemical analysis/X-ray photoelectron spectroscopy (ESCA/XPS), which can chemically characterize the surface regions. A combination of morphological and chemical information can help improve research and analysis.

The purpose of the present study was to apply these complementary techniques to determine whether a LTP treatment changes the surface chemistry and morphology of APMP fiber. A further goal was to discover the fundamental mechanisms of developing the strength properties for plasma-treated APMP fibers.

EXPERIMENTAL

Materials

The eucalyptus APMP fibers were purchased from the paper-making branch office of Nanning Sugar Industry Co., Ltd (China). The pulp was manufactured from eucalyptus

and intended for use in paperboard products. The pulp had a freeness of 750 CSF (mL) and a brightness of 73.3% ISO. The fibers were shown to contain 60.09% cellulose, 16.08 pentosan, 22.98% Klason lignin, and 0.35% extractives. The ash was 1.72%. They were processed by air drying. After processing, they were hermetically packaged and stored at 4 °C.

Methods

Low-temperature plasma treatment (LTP)

LTP was generated from HPD-100B equipment operating as a sub-atmospheric glow discharge system (Nanjing Suman Electronics Co., Ltd., China). This system is able to generate a stable electric power discharge of about 84 watts (0.56 amps of electricity current and 150 volts). The schematic representation of the experimental setup for LTP treatment is shown in Fig. 1. The LTP was applied to sample sheets, which were placed on the lower ground electrode. Air and oxygen were used as the discharge gases. When the pulps were processed, a mixture of air and oxygen in a volume ratio of 5:2 was introduced into the system. The treatment lasted for two minutes at a pressure of 1000 Pa.

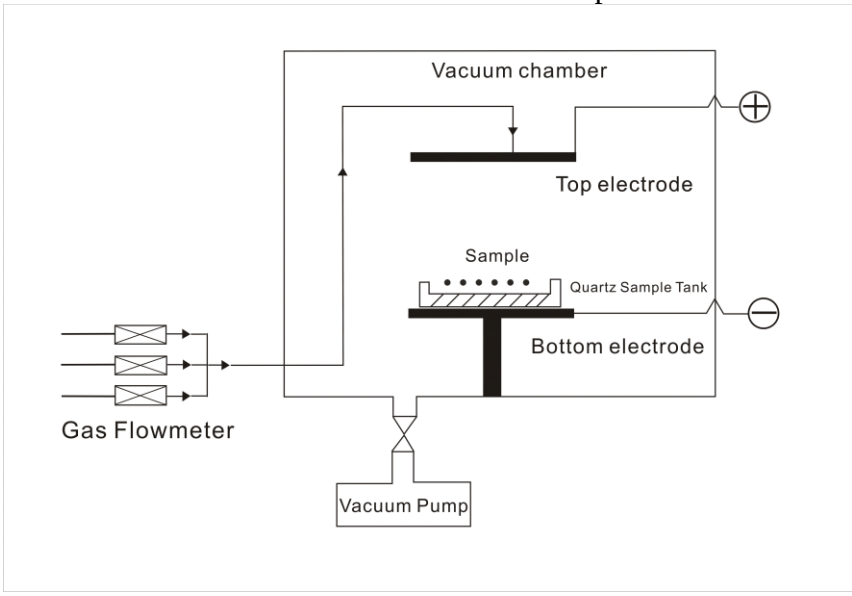

Fig. 1. Schematic representation of the experimental setup for LTP treatment.

AFM analysis

Measurements were performed using an AFM (Agilent 5500, Keysight Technologies, USA). The untreated and treated eucalyptus fibers, each with a pulp concentration of 2%, were put into standard fiber disintegrator and defiberized at 6000 revolutions/min. A select amount of dispersed fibers was dropped onto the mica plate and dried before AFM investigation. The images were scanned using the tapping mode on a scanning area of about 3 μm × 3 μm. Images of at least 10 different fibers were scanned, for each sample, at three different locations on each fiber.

ESCA analysis

The ESCA measurements were carried out using a Labmk II scanning photoelectron spectrometer (VG Scientific, UK). The MgKα X-ray emitter operated at 1245 eV, 150 W, under a working vacuum of $10^{-4} \times 10^{-6}$. Protactinium (Pa) was used to

excite the samples, which were dried before being examined. In order to average the heterogeneity of the sample, survey scans and high-resolution regional spectra were recorded from at least three measurement points in each sample.

RESULTS AND DISCUSSION

Surface Morphology of Plasma Treated Fiber

Atomic force microscopy has become a valuable analytical tool for investigating the surface of fibers. When the probe of the AFM connects with the fibers, the force between the probe's tip and the fibers causes a displacement of the AFM's cantilever, at which point the photoelectric detector generates laser displacement. The resulting voltage change corresponds to the deformation of the cantilever; it is from this correspondence that cantilever deformation measurements are obtained. There are three operating modes for an AFM: contact mode, noncontact mode, and tapping mode. In contact mode, the tip which scans the sample will have a close contact with sample surface, so the force between tip and samples is repulsive, and this mode cannot be applied to soft samples. In noncontact mode, there are attractive interatomic forces between the tip and the sample. But under this mode, the contaminant layer on the samples will interfere the cantilever oscillation and make the diagrams have low resolution (Boussu *et al.* 2005). The tapping mode is commonly used to detect the fibers and to reveal the topography of the sample surface. In this mode the phase diagram can be created by detecting the phase lag of the cantilever oscillation relative to the signal sent to the piezo driving the cantilever (Gao and Mäder 2002; Wang and Hahn 2007). As the AFM were equipped with a hydrophilic silicon tip, the interaction between the tip and the sample can be detected to deduce the sample is hydrophilic or hydrophobic. Hydrophilic surface interacts strongly with a hydrophilic tip, resulting in a large phase shift. On the contrary, a hydrophobic surface interacts faintly with the tip so that a little phase shift will be apparent in the result.

The phase diagram can reflect many details and features that do not come out in the topographic diagram (Huang *et al.* 2009). Each component's level of hydrophilicity can be estimated by analyzing the change in brightness of the phase diagram. Cellulose will display as a dark tone in the AFM phase diagram, indicating that it is a hydrophilic substance, and it will form a low-phase area within the phase diagram. On the contrary, lignin will display as a light tone, indicating it is a hydrophobic substance, and it will form a high-phase area within the phase diagram (Simola *et al.* 2000; Gustafsson *et al.* 2003). Börås *et al.* showed that the extractives and lignin cover the carbohydrates as globular shapes in AFM diagrams. The lignin appears on the surface as irregular flakes (Börås and Gatenholm 1999).

The AFM diagrams in Fig. 2 and Fig. 3 contrast untreated fibers and LTP-treated fibers. Both the topographic and phase diagrams of untreated and treated fibers are shown in each figure.

The scan range for untreated fibers was set at 3μm × 3μm. As can be seen in Fig 2(a) and Fig 2(b), a layer of spherical particles with a lot of regular and irregular granule shaped hydrophobic granules appeared on the surface of fiber. This may attributed to the extractives and lignin wrapped around the surface of the fibers (Maximova *et al.* 2001; Koljonen *et al.* 2004).

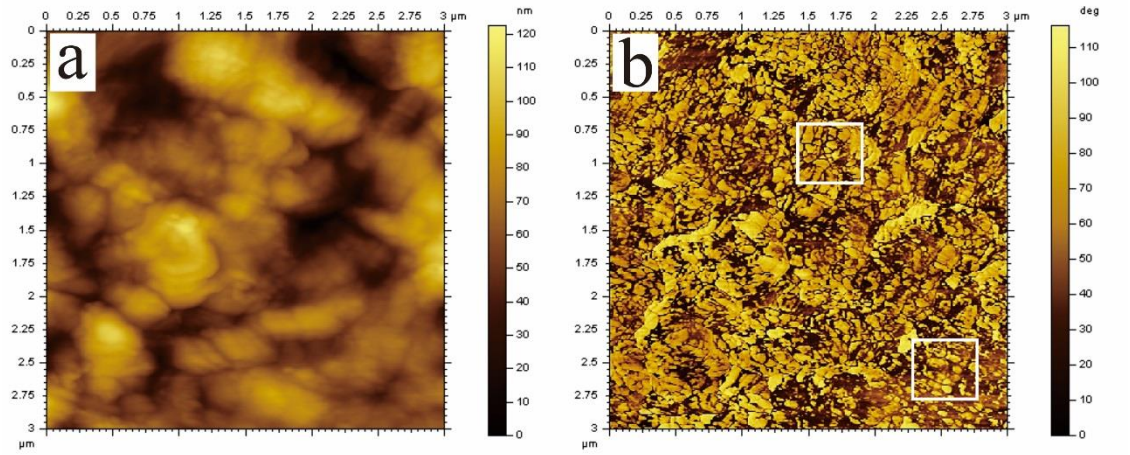

Fig. 2. AFM images of untreated eucalyptus APMP fibers: (a) topographic image, (b) phase image

Figures 3(a) and 3(b) show the AFM diagrams of eucalyptus APMP fibers after LTP treatment. These diagrams show that the granular structure of the fiber surface was reduced after the LTP treatment, and the exposed bottom structure was the characteristic orientation angle of S1 layer of fibrillar structures of about 50º to 70º. The structures appear to imply that the LTP treatment could remove the thin P layer outside of the fiber, but the surface was still partly covered by irregular granular materials. This could be explained by the etching effect due to LTP treatment, in which process the lignin and extractives components were oxidized and removed. Consequently, the hydrophobic substances on the fiber surface are reduced, and more hydrophilic fiber components are exposed. Similar results were reported in some previous studies (Gustafsson 2003; Lorraine 2005).

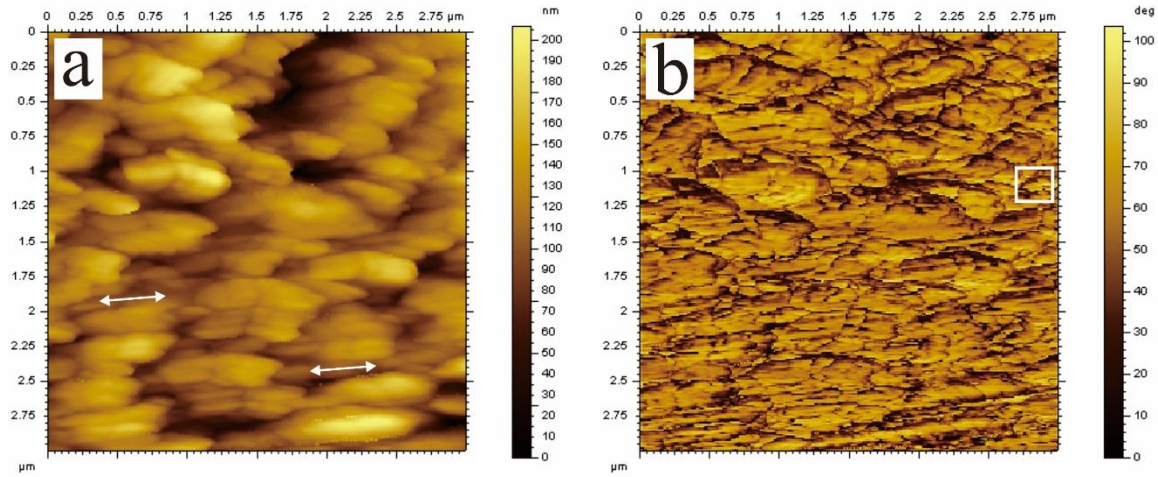

Fig. 3. AFM images of LTP-treated eucalyptus APMP fibers: (a) topographic image, (b) phase image

Since several wood constituents in APMP pulps such as pectin, xylan, and extractives were unable to be identified by AFM, benzol-alcohol extraction was used to remove contaminants and surface extractives on LTP treated fibers and then disclose more

information about the components change. Figures 4(a) and 4(b) show the AFM images of eucalyptus APMP fibers treated by LTP after extraction of benzol-alcohol. Figure 4(a) clearly shows that the orientation angle of the fibrils was about 50° to 70°, which provides evidence that S1 of secondary walls were separated. Figure 4(b) shows that, after the extraction of benzol alcohol, some of the particles and bulk material initially over the surface of APMP fibers were reduced, and the surface of the fibers became relatively smooth. The wood resin (extractive) was mainly removed (usually including terpenes, resin acid, fatty acid and its ester, ethanol, hydrocarbons, and other neutral compounds), while the lignin was mostly retained. These results were similar to Vander Wielen's suggestion (2005) that the DBD treatment of unextracted fibers removes surface extractive and/or lignin. Therefore, it was possible to speculate that the regular granular material observed in the AFM phase diagram of APMP fibers was mainly lignin. It was also further indicated that LTP treatment mainly acted on the lignin covering the surface of the fiber, which had been confirmed in some studies in XPS.

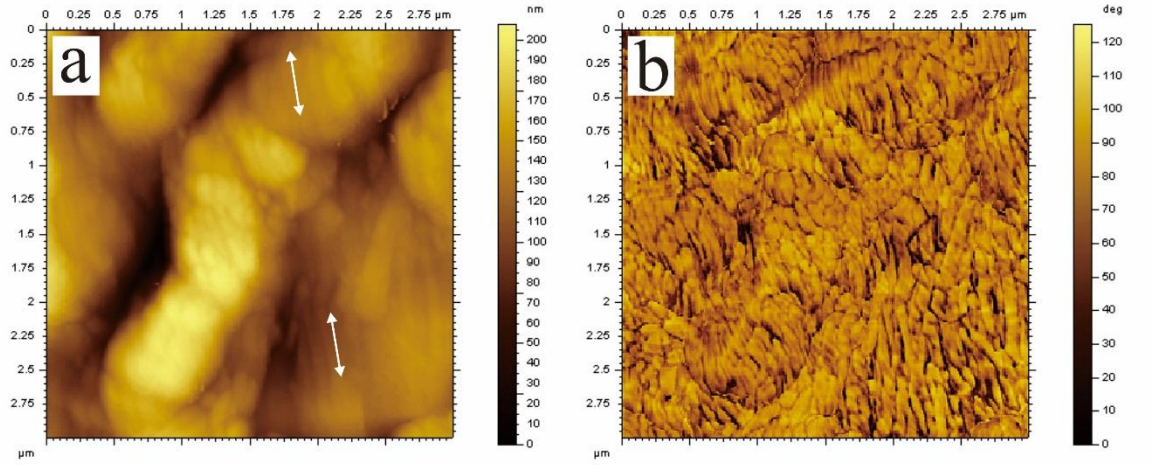

Fig. 4. AFM images of eucalyptus APMP fibers treated by LTP after extraction: (a) topographic image, (b) phase image

Surface Chemistry of Plasma-Treated Fiber

As a surface analysis technology, ESCA can identify the structure and analyze the qualitative and quantitative state of the solid surface by measuring the energy distribution of electrons irradiated by X-rays. In the field of pulping and papermaking, ESCA technology can be used to characterize the lignin, extractives, carbohydrates, and other chemical components on the fiber surface. The presence of these components can influence the binding strength between paper fibers, and they also can affect the physical properties of the paper (Zhang *et al.* 1994; Suurnäkki *et al.* 1996; Barzyk *et al.* 1997).

Among the elemental components of pulp fibers, only carbon and oxygen can be analyzed by ESCA. There are four binding modes for carbon on the fiber surface: C1, C2, C3, and C4 (Johansson 2002; Koljonen *et al.* 2003). C1 stands for carbon atoms that attach only to carbon or hydrogen (-C-C-or-C-H). These are mainly from lignin and extractives (Dorris and Gray 1978; Li and Reeve 2004). C2 represents carbon atoms that are single-bonded to one oxygen atom (-C-O). These are found in hydroxyl from cellulose and hemicellulose. C3 refers to carbon atoms that are bonded with one carboxide oxygen atom

or with two single-bond oxygen atoms (C=O or O-C-O). C4 stands for carbon that is single-bonded to one oxygen atom and double-bonded to another oxygen atom (-COOH).

Figure 5 compares the scanning spectra of LTP-treated APMP fibers and untreated fibers. Table 2 shows the percentage of each element in LTP-treated APMP fibers and untreated fibers.

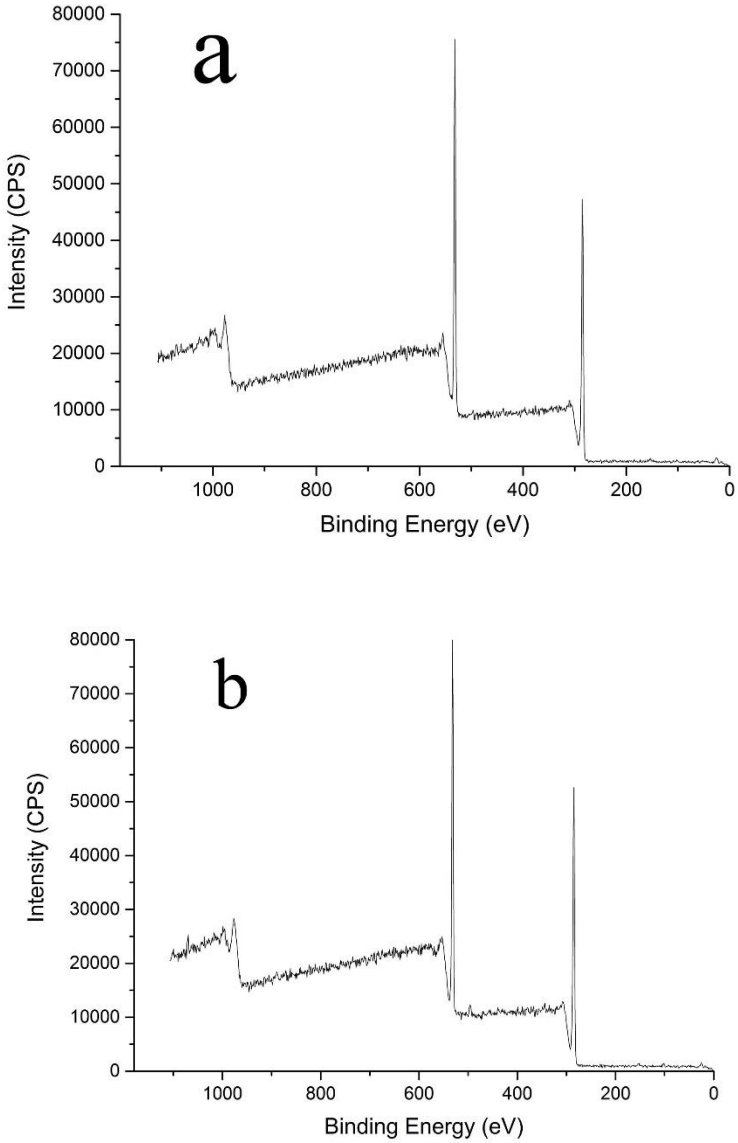

Fig. 5. The scanning spectra of LTP-treated APMP fibers and untreated fibers: (a) Untreated fibers, (b) Treated fibers

In the binding energy of 280 to 290 eV and 530 to 534 eV, there were strong absorption peaks, which indicate the presence of carbon and oxygen on the surface of the eucalyptus APMP fibers.

As shown in Table 1, after treatment, the oxygen to carbon ratio increased from 50.08% to 55.47%. That the oxygen content of the fiber increased after air or oxygen LTP treatment, also means that the carbohydrate content increased. Since oxygen atoms are

present only in modes C2, C3, and C4, the increase in the oxygen peak area corresponds to a decrease in the peak area of C1. So in conclusion, the LTP treatment can reduce the content of lignin and extractives, and result in more carbohydrates at the surface.

Table 1. Surface Elementary Composition of APMP Fiber before and after Treatment

Samples	Atomic composition		
	C (1s)(%)	O (1s)(%)	O/C ratio(%)
Untreated fibers	66.63	33.37	50.08
Treated fibers	64.32	35.68	55.47

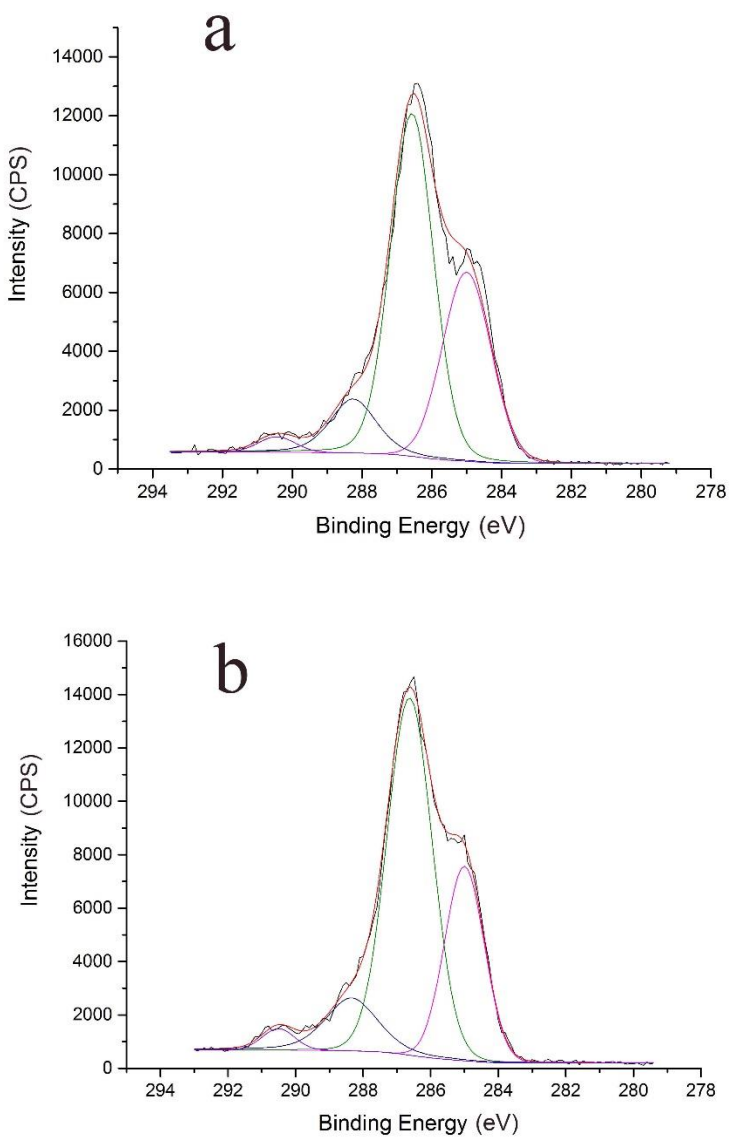

Fig. 6. ESCA C1's spectra of untreated and treated APMP fiber surfaces: (a) untreated fibers, (b) treated fibers

Figures 6(a) and 6(b) show the C1's spectra of untreated and treated APMP eucalyptus fiber surfaces. As can be seen, the C1's fiber peaks include four peaks, as identified as C1, C2, C3, and C4.

Table 2. Binding Energy and C1's Peak Area Ratio of APMP Surface

Samples	Untreated fibers			Treated fibers		
	Binding energy (eV)	Peak Area	Proportion (%)	Binding energy (eV)	Peak Area	Proportion (%)
C1	285.000	11191.300	32.54	285.000	10747.830	27.39
C2	286.573	18983.540	55.20	286.625	23004.300	58.63
C3	288.255	3525.955	10.25	288.346	4505.240	11.48
C4	290.442	688.643	2.01	290.507	978.818	2.50

Table 2 shows that the peak area ratio of C1 decreased from 32.54% to 27.39%. This may be the result of LTP treatment acting on the fiber surface (*i.e*., etching it), so that the lignin and extractives content on the fiber surface decreased. The peak area ratio of C2 was enhanced from 55.20% to 58.63%. This may be due to the effect of LTP treatment, more hydroxyls have been exposed on fibers surface. The peak area ratio of C3 increased from 18.76% to 21.03%. These may indicate that the C-C, C-H, or C-O chemical bonds ruptured and new C=O or O-C-O chemical bonds were created after LTP treatment, and that more carbohydrates were generated on the surface of fibers. The ratio of C4 improved from 2.01% to 2.50%. This may be the content of carboxyl changed after LTP treatment.

CONCLUSIONS

1. The regular and irregular hydrophobic materials that cover the surface of fibers can be identified in AFM diagrams as sphere-like particles. After low-temperature plasma (LTP) treatment, the spherical particles on the fiber surface decreased, exposing the S1 layer, which is rich in cellulose microfibrils, on the fibers' surface.
2. ESCA was used to analyze changes in the surface oxygen to carbon ratio, and the surface carbon valence of alkaline peroxide mechanical pulp (APMP) fibers. After LTP treatment, the oxygen to carbon ratio of the fiber surface had significantly increased, while the peak area of C1 declined, as a result of the increased surface exposure of hydrophilic groups, and the generation of carbohydrate content at the surface. Additionally, lignin and extractives had been removed from the eucalyptus fibers' surface, and the S1 layer, which is rich in microfibrils, had been exposed.

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