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Changes of anionic groups in alkaline peroxide-impregnated aspen chemithermomechanical pulp during subsequent alkaline peroxide bleaching

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ABSTRACT

The effect of alkaline peroxide bleaching on the total anionic groups (AGs) and surface AGs in aspen chemithermomechanical pulp (CTMP) fibers was investigated. Alkaline treatment, especially alkaline peroxide bleaching resulted in the formation of new AGs and surface AGs in the CTMP fibers. The carboxylic groups in uronic acid units, including 4-*O*-methylglucuronic acid, galacturonic acid, and glucuronic acid units were the main contributors to the AGs in the fibers. However, the oxidized lignin accounting for more than 30% of the total AGs in the bleached CTMP fibers, was the main origin of the new AGs formed during the peroxide bleaching. In addition, the new AGs were also formed by extensive deesterification of the residual esterified uronic acids in pectins and lignin-carbohydrate complexes (LCCs). Although some uronic acid units were dissolved in the process water, both the total AGs and surface AGs in the fibers increased after alkaline peroxide bleaching.

1. Introduction

Anionic groups (AGs) can originate from the wood used as raw material in pulp manufacture or be generated during pulping, bleaching, and papermaking (Sjöström, 1989), which are the most important groups in pulp because they can significantly affect fiber swelling, beatability, paper strength properties, and interactions with paper chemicals (Barzyk, Page, & Ragauskas, 1997; Fardim, Moreno, & Holmbom, 2005; Konn, Pranovich, Fardim, & Holmbom, 2007; Laine & Stenius, 1997; Zhang, Sjögren, Engstrand, & Htun, 1994). Carboxyl groups are the main AGs present in all papermaking fibers. In native wood, most of the carboxyl groups originate from uronic acid units. In both softwood and hardwood, the main uronic acids are 4-O-methylglucuronic acid units bound to xylans and galacturonic acid units in pectins (Willför, Sundberg, Hemming, & Holmbom, 2005; Willför, Sundberg, Pranovich, & Holmbom, 2005).

During pulping and alkaline peroxide bleaching of CTMP, new AGs can be formed, and bleached CTMP contains more AGs than any other papermaking fibers (Fardim, Moreno, & Holmbom, 2005). The formation of new AGs during pulping and bleaching of CTMP depends on the wood materials and process conditions. Pectins are the important wood components to form new AGs during CTMP pulping and bleaching, because they can form new free uronic acids by deesterification under alkaline conditions. In addition, the pectins can also be degraded by polygalacturonic chain-splitting according to the β-elimination mechanism under alkaline conditions (Kiss, 1974; Renard & Thibault, 1996). The degraded pectins form new uronic acid units in the fibers or dissolve in the process water during pulping and bleaching of CTMP. The degradation and dissolution of pectins depends on the pretreatment conditions. About 2%–10% of the total pectins in the wood were dissolved in the process waters during CTMP pulping (Konn, Pranovich, & Holmbom, 2006). The alkalinity is the most important factor that affects the deesterification of pectins during impregnation stage in CTMP pulping. In the alkaline peroxide impregnation stage of spruce chips, increasing NaOH dosage from 1% to 2% could result in the deesterification of pectins from 50–60% to 70–80% (Konn et al., 2006). Hafrén and Daniel (2003) reported that the deesterification of pectins was not complete during CTMP pulping of spruce, and the residual esterified galacturonic acid units were specifically localized on the surface of unbleached CTMP. In addition, it was believed that new AGs could also be created in the fiber materials duo to lignin oxidation in the alkaline peroxide impregnation of spruce CTMP (Konn et al., 2007).

The AGs would no doubt be influenced by the subsequent alkaline peroxide bleaching. The AGs content in thermomechanical pulp (TMP) increases during peroxide bleaching, which is the results of deesterification of esterified uronic acid units in pectin and lignin-carbohydrate complexes (LCCs), and the generation of new carboxyl groups during lignin oxidation (Pranovich, Sundberg, & Holmbom, 2003). The study by Fardim and Holmbom (2005) showed that the main origins of AGs are the 4-*O*-methylglucuronic

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acid units, galacturonic acid units, sulfonic acid groups and oxidized lignin in the alkaline peroxide bleached CTMP from spruce and aspen. However, the changes of AGs and surface AGs in the fibers of CTMP during alkaline treatment and alkaline peroxide bleaching have not been well understood.

Nowadays, fast-growing aspen such as *Populus* × *euramericana* 'Guariento' or *Populus* × *euramericana* 'Neva' is regarded as one of the most suitable hardwood species grown in North China. The aspen has been widely planted and the use in the kraft and mechanical pulp production has increased in China in recent years (Xu et al., 2010). Many Chinese pulp and paper mills including Huatai, Sunpaper and Tralin have already established large aspen plantations and several modern production lines of aspen bleached CTMP (Yang, Lu, & Ni, 2006).

The aim of this study was to investigate the origin, formation and changes of total and surface AGs in fibers during the only alkaline treatment and alkaline peroxide bleaching of aspen CTMP. The dissolution of uronic acid units, the extensive deesterification of uronic acid units and the oxidation of lignin during alkaline peroxide bleaching of aspen CTMP were discussed in detail.

2. Experimental

2.1. Materials

Aspen (a mixture of *Populus* × *euramericana* 'Guariento' and *Populus* × *euramericana* 'Neva') unbleached CTMP was prepared in Huatai Group (Dongying, China). The aspen chips were steamed for 30 min at 100 °C after being washed thoroughly. The compressed chips were impregnated in the liquor of 2.5% H_2O_2 (on o.d. wood), 3% NaOH (on o.d. wood) and 2.5% Na_2SiO_3 (on o.d. wood) at 85 °C for 30 min and then subjected to two-stage refining. First stage refining was carried out at a conical-disc refiner (RGP 82 CD, Metso), which disc diameter is 2080 mm, and the second stage refining was carried out at a single-disc refiner (RGP 268 SD, Metso), which disc diameter is 1728 mm. The refined pulp was washed and then concentrated to about 20% consistency before use. The pH of the pulp was 8.3 and no residual peroxide was found in the pulp. All chemical reagents used in the experiment were analytic grade.

2.2. Alkaline peroxide bleaching

The peroxide bleaching was conducted in plastic bags in a thermostatic water bath under the following conditions: 4.0% H_2O_2 (on o. d. pulp), 3.0% NaOH, 3.0% Na_2SiO_3, 0.05% $MgSO_4$, 10% pulp consistency, 70 °C and 90 min. At the end of the bleaching, the pulp was washed twice with deionized water in a Buchner funnel with a 200-mesh screen. For the alkali-treated pulp, the pulp was treated as peroxide bleaching process, but no H_2O_2 was added.

2.3. Extraction

The unbleached, alkali-treated and bleached pulps were extensively washed with distilled water at 60 °C to remove all dissolved and colloidal substances. It was then extracted with acetone–water (9:1, v/v) to remove extractives and then washed with EDTA and 0.01 M HCl solution to remove metal ions (Fardim et al., 2005).

2.4. Conversion of AGs to sodium salt form

The AGs were converted to sodium form by treatment with 2 mM $NaHCO_3$ solution and stirring for 30 min followed by filtration. The pulps were then washed with deionized water until the conductivity of the filtrate was lower than 5 μS cm^{-1}. The fully washed pulps were then used for MB (methylene blue) sorption to measure the AGs (Fardim et al., 2005).

2.5. MB sorption

MB sorption method, which is based on the replacement of AG counter-ions by the cationic dye, was used for determination of the total AGs content (Fardim & Holmbom, 2003). About 100 mg of o.d. pulp was used for every test and a sorption time of 20 min at 500 rpm agitation was used.

2.6. Determination of uronic acid units in fibers

The uronic acid units in the fibers were determined by gas chromatography (GC) after methanolysis as described by Sundberg, Sundberg, Lillandt, and Holmbom (1996). All the results were calculated on an extractive-free and freeze-dried pulp basis.

2.7. XPS analysis

The surface AGs were determined by XPS analyses on MB-labeled samples. X-ray photoelectron spectra of fiber surfaces were obtained with Thermo Scientific K-Alpha XPS spectrometer (ThermoFisher Scientific, East Grinstead, UK) with a monochromatic Al Kα X-ray source. The samples were run at a take-off angle (relative to the surface) of 90°, and the analyzed area was 400 μm × 400 μm. Charge compensation was provided by utilizing the flood gun provided with the instrument. Low resolution (pass energy 150 eV) was used for survey spectra and characterization of the fiber surface elements composition. The relative concentrations of C, O, S, and N (in at.%) on the fiber surfaces were measured using a pass energy of 150 eV in a snapshot mode, collection time optimized for signal-to-noise. The estimation of surface AGs was calculated according to Eq. (1) by Fardim et al. (2005).

$$\mathrm{SAG} = \left[\frac{\mathrm{S}\times 32.06}{\mathrm{C}\times 12.00 + \mathrm{O}\times 15.99 + \mathrm{N}\times 14.00 + \mathrm{S}\times 32.06}\right] \times \left[\left(\frac{1}{32.06}\right)\times 10,000\right] \quad (1)$$

2.8. Distribution of AGs by ToF-SIMS imaging

The pulps after extraction and metal ions removal were treated with 2 mM $MgCl_2$ with stirring for 30 min, and then the pulps were washed with the deionized water until the conductivity of the final filtrate was less than 2.0 μS cm^{-1}.

The surface distribution of AGs was analyzed using ToF-SIMS imaging by monitoring the distribution of characteristic Mg^{2+} on a raster size of 200 μm × 200 μm. All measurements were conducted on a ToF-SIMS IV (Münster, Germany). A Bi liquid metal ion gun was used and spectra were obtained in a high spatial resolution mode (Sodhi, 2004) using the Bi_3^+ cluster as the primary ion species.

3. Results and discussion

3.1. Total AGs and uronic acid units in fibers

MB sorption method was reported to be a straight-forward and repeatable method for total AGs of the fibers (Fardim & Holmbom, 2003). Because the wood chips were impregnated with alkaline peroxide instead of alkaline sulfite in the study, the sulfonic acid group did not exist in CTMP used. As shown in Table 1, the amount of AGs in the unbleached CTMP fibers was 195 μmol/g. Alkali treatment and alkaline peroxide bleaching increased AGs to 230 μmol/g and 275 μmol/g, respectively. That is to say, alkali

Table 1
The total AGs determined by MB sorption and sugar units by GC analysis in the fibers of the pulps (μmol/g).

Pulps	Rha	Ara	Xyl	Man	Gal	Glu	GlcA	GalA	MeGlcA	Total uronic acid units	Total AGs
Unbleached	35	37	1230	82	56	184	17	87	128	233	195
Alkali-treated	32	36	1150	78	55	180	18	70	118	206	230
Alkaline peroxide bleached	29	32	958	64	49	154	16	74	102	192	275

Rha, rhamnose; Ara, arabinose; Xyl, xylose; Man, mannose; Gal, galactose; Glu, glucose; GlcA, glucuronic acid; GalA, galacturonic acid; MeGlcA, 4-*O*-methylglucuronic acid.

treatment and alkaline peroxide bleaching resulted in the formation of 18% (35 μmol/g) and 41% (80 μmol/g) new AGs in CTMP fibers. Obviously, uronic acid units such as 4-*O*-methylglucuronic acid (MeGlcA), galacturonic acid (GalA) and glucuronic acid (GlcA) units were the main origin of the AGs in the pulp fibers. MeGlcA from 4-*O*-methyl glucuronic acid-xylan and GalA from pectins were the major contributors to the uronic acid units in the pulps.

The results in Table 1 also showed that MeGlcA and GalA units, as well as the neutral sugar units especially for xylan in the fibers decreased after alkali treatment or alkaline peroxide bleaching, which was due to the dissolution of polysaccharides at alkaline conditions (Hanneman, Hrutifiord, & McKean, 2001; Konn et al., 2006; Pranovich et al., 2003; Sundberg et al., 1996). The possible sources of AGs in the pulps are the free carboxylic groups in uronic acid units and oxidized lignin. The total uronic acids measured by GC decreased after alkali treatment, and no oxidized lignin was formed during alkali treatment, so it seemed that the total AGs in alkali-treated pulp should be less than the total AGs in unbleached pulp. However, the amount of total AGs in the fibers shown in Table 1, increased after alkali treatment. This contradiction should be due to the extensive deesterification of esterified uronic acid units such as the esterified pectins and the esterified uronic acid units in LCCs under alkaline conditions. In native wood, part of the lignin is linked by ester bonds to 4-*O*-methylglucuronic acid units and form LCCs (Eriksson, Goring, & Lindgren, 1980). The ester bonds in LCCs between lignin and 4-*O*-methylglucuronic acid units in xylans are ready to be split at alkaline conditions (Eriksson et al., 1980; Obst, 1982), so they were partly split in alkaline peroxide impregnation of wood chips during CTMP pulping (Konn et al., 2006). The residual esterified uronic acid units, that survived the impregnation stage, would be deesterified in subsequent alkaline peroxide bleaching of CTMP and the new carboxylic groups were formed. The amount of new carboxylic groups formed by deesterification of pectins and esterified uronic acid units in the residual LCCs in pulp was more than that of the uronic acid units dissolved in the process water at alkaline conditions. Therefore, the total AGs in the fibers increased after alkali treatment or alkaline peroxide bleaching.

When the sugar units are determined with acid methanolysis followed by GC analysis method, the esterified uronic acid units such as the methylated pectins which cannot contribute to the total AGs in CTMP fibers are also determined as galacturonic acid units (Willför et al., 2005a; Willför et al., 2005b). Therefore, the amount of the total AGs in fibers of the unbleached CTMP measured by MB sorption method (195 μmol/g) were much less than the total uronic acid units determined by acid methanolysis followed by GC analysis method (233 μmol/g), even though the AGs in the oxidized lignin were not taken into account.

The GalA in peroxide-bleached pulp was slight more than that in alkali-treated pulp, and it was perhaps due to the lower alkalinity in peroxide pulp system than that in alkaline treatment pulp system, which is caused by the dissociation of peroxide and the formation of carboxylic groups during peroxide bleaching. The degradation of the polygalacturonic acid units caused by beta-elimination is less at lower alkalinity during peroxide bleaching, which causes less dissolution of polygalacturonic acid units.

It is assumed that the residual esterified uronic acid units in pectins and LCCs of unbleached CTMP are completely deesterified during alkali treatment or peroxide bleaching (Pranovich et al., 2003), and the dissolution of the oxidized lignin formed in the chip impregnation can be neglected during the alkali treatment (some oxidized lignin formed in the impregnation has been dissolved and washed out during the pulping). In alkali-treated pulp, the sources of AGs were the free carboxylic groups in uronic acids and oxidized lignin. Based on the assumptions, the AGs originated from oxidized lignin (24 μmol/g) in alkali-treated pulp could be obtained

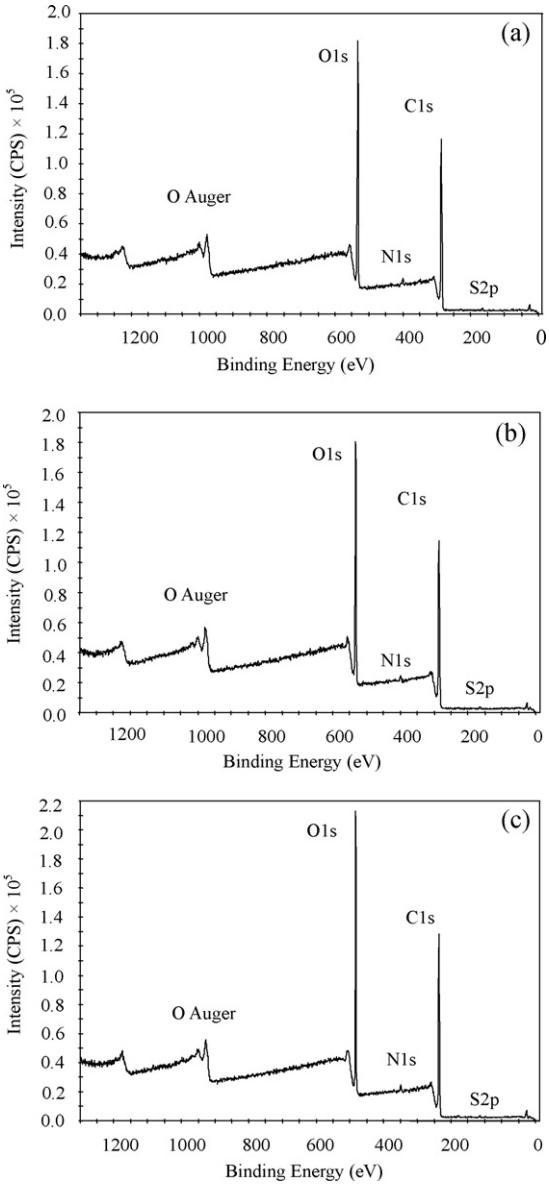

Fig. 1. X-ray photoelectron spectra of MB-labeled unbleached (a), alkali-treated (b) and peroxide bleached CTMP (c) samples at low resolution.

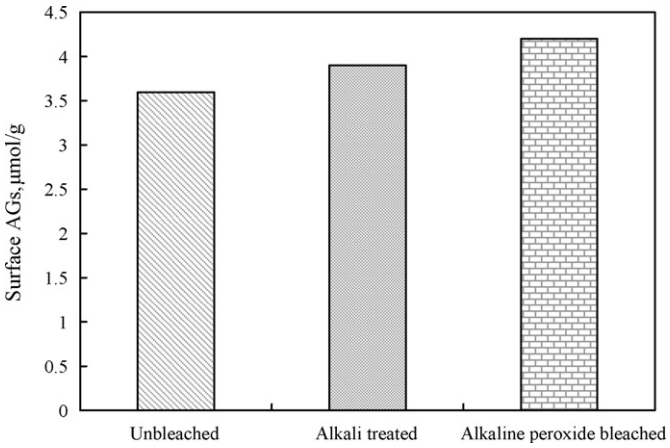

Fig. 2. The surface AGs of MB-labeled fibers measured by XPS.

by subtracting the total uronic acids (206 μmol/g) from the total AGs measured by MB sorption (230 μmol/g).

In unbleached pulp, which was pre-treated with alkaline peroxide in impregnation stage during CTMP pulping, the sources of AGs were also the free carboxylic groups in uronic acids and oxidized lignin. Based on the assumptions, the AGs originated from oxidized lignin in unbleached pulp was the same as that in alkali-treated pulp. The free carboxylic groups in uronic acids (171 μmol/g) in unbleached pulp could be obtained by subtracting the carboxylic groups in oxidized lignin (24 μmol/g) from the total AGs (195 μmol/g). So the content of esterified uronic acid units (62 μmol/g) in unbleached pulp was obtained by subtracting the free carboxylic groups in uronic acids (171 μmol/g) from the total uronic acid units measured by GC (233 μmol/g). It could be deduced that the esterified uronic acid units in the unbleached CTMP account for more than 25% of total uronic acid units. The extensive deesterification of the residual esterified uronic units would occur during alkaline peroxide bleaching of CTMP, which caused the formation of new AGs in the fibers.

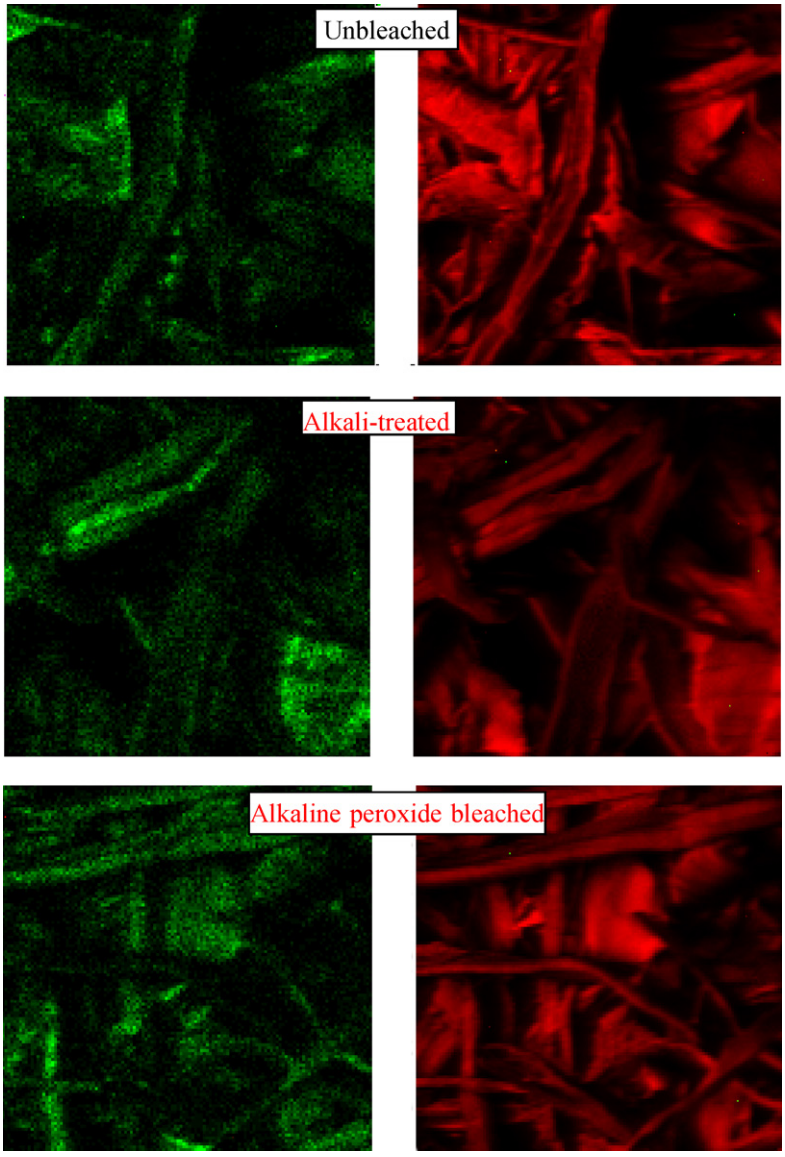

Fig. 3. Total ions (right) and Mg ions (left) images of unbleached, alkali-treated and peroxide bleached CTMP surfaces labeled with Mg^{2+}. The raster size was 200 μm × 200 μm; scale of 100 μm, positive mode ToF-SIMS.

In addition, parts of carboxylic groups formed in lignin by oxidation in alkaline peroxide impregnation also contribute to the total AGs of fibers (Konn et al., 2007). Compared to the alkali-treated pulp, the lignin oxidation in alkaline peroxide bleaching resulted in the higher AGs content in the alkaline peroxide bleached pulp. The gap (83 μmol/g) between the total AGs (275 μmol/g) and the total carboxylic acid in uronic acids (192 μmol/g) in the bleached pulp should be regarded as the AGs originated from the oxidized lignin in the bleached CTMP. Therefore, the new AGs formed by oxidation of lignin in the alkaline peroxide bleaching contributed to 59 μmol/g. Obviously, the new AGs formed by lignin oxidation contained 74% of the total new AGs (80 μmol/g) formed during the alkaline peroxide bleaching of aspen CTMP. The AGs (83 μmol/g) in the fibers originated from the oxidized lignin that formed both in alkaline peroxide impregnation and in bleaching of CTMP accounted for more than 30% of the total AGs in the bleached CTMP.

The deesterification of the residual uronic units in LCCs and the degradation of polygalacturonic chain by the β-elimination mechanism would cause the dissolution of uronic acids units of the unbleached CTMP fibers under the alkaline conditions. From the data of the total uronic groups of the pulps in Table 1, it was also deduced that 12% and 18% of the total uronic acid units in the CTMP fibers were dissolved in process water during the only alkali treatment and the alkaline peroxide bleaching, respectively. The dissolved uronic acids units could be one of the sources of the anionic trash in process water.

3.2. Surface AGs by XPS analysis

The detection of surface AGs is much dependent on the analytical method used. The proximate analysis depth of XPS technique for fiber surface is 3-10 nm, corresponding to about 0.1% of fiber cell wall width (Fardim & Holmbom, 2005). Fig. 1 was the X-ray photoelectron spectra of MB-labeled pulp samples at low resolution. The surface AGs were calculated according to the concentration of C, O, S, and N (in at.%) on the fiber surfaces, and the results are shown in Fig. 2. The surface AGs in the fibers of the unbleached, alkali-treated and bleached CTMP were 3.6 μmol/g, 3.9 μmol/g and 4.2 μmol/g, respectively. In the wood materials, pectins are localized between fibers (Hafrén & Westermark, 2001). After fiber separation by mechanical pulping, some methylated pectins are exposed at the fiber surface (Hafrén & Daniel, 2003), and the extensive deesterification of pectins would occur at alkaline conditions. Therefore, the origin of new surface AGs in the fibers of alkali-treated pulp was the formation of free carboxylic groups in galacturonic acids by extensive deesterification of pectins on the surface of the fibers at alkaline conditions. The alkaline peroxide bleaching resulted in more surface AGs than alkali treatment, which should be due to the formation of new AGs in the surface of the fibers by lignin oxidation.

3.3. Surface distribution of AGs by ToF-SIMS imaging

Time of fight-secondary ion mass spectroscopy (ToF-SIMS) can be used as an assisted tool for studying the distribution of surface AGs of the fibers (Fardim & Holmbom, 2005; Orblin & Fardim, 2010). The distribution of AGs at the surface of fibers could be analyzed with ToF-SIMS imaging by monitoring the distribution of characteristic Mg^{2+} labeled on the surface of the fibers. It could be seen from the Fig. 3 that a patchy distribution of AGs on the fiber surface of all pulps was observed. Compared to the unbleached CTMP and alkali-treated CTMP, more uniform distribution of AGs on the fiber surface of bleached CTMP was observed, which was perhaps due to the formation of carboxyl groups by lignin oxidation.

4. Conclusions

Alkaline treatment, especially alkaline peroxide bleaching of aspen CTMP could result in the formation of new AGs and surface AGs in the fibers. The uronic acids units, including 4-*O*-methylglucuronic acid, galacturonic acid, as well as glucuronic acid units were the main origin of the AGs in the pulp fibers.

The oxidized lignin was another important contributor to the AGs in the peroxide bleached CTMP. The oxidized lignin was formed during alkaline peroxide impregnation of wood chips and pulp bleaching. The AGs in the fibers originated from the oxidized lignin in the bleached CTMP could account for more than 30% of total AGs in the fibers. However, the new AGs formed by lignin oxidation contained 74% of the total new AGs formed during the alkaline peroxide bleaching of the CTMP.

Some uronic acid units in the CTMP fibers were dissolved during the alkaline peroxide bleaching, but much more new AGs in the fibers were formed by extensive deesterification of the residual esterified uronic acids in pectins and LCCs, and the lignin oxidation during the alkaline peroxide bleaching. Therefore, the total AGs of the CTMP fibers increased after the peroxide bleaching.

Alkaline peroxide bleaching could increase the surface AGs in fiber by 17%, due to the deesterification of the esterified uronic units and lignin oxidation at the fiber surface.

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