DEGRADATION AND STABILITY OF PULP TREATED IN HETEROGENEOUS AND HOMOGENEOUS PHASES

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This study aims to investigate the degradation and stability of pulp treated in heterogeneous and homogeneous phases. The results showed that the homogeneous system 1-Allyl-3-Hexylimidazolium chloride (AHIMCl) ionic liquid exhibited special dissolubility for pulp samples, but showed lower thermal stability than the heterogeneous treatments by 20 wt% NaOH or 2-ethanediamine (EDA) solution. Compared with the 20 wt% NaOH solution, the 20 wt% EDA solution and AHIMCl treatments had special decrystallizing ability, and the 20 wt% EDA solution had lower reductions in the mean degree of polymerization of pulp after the treatments for 72 h at 5 ^{o}C. X-ray diffractogram (XRD) analysis showed that after the AHIMCl and 20 wt% EDA solution treatments, the 002 crystal plane size of the treated pulp samples (＜1 nm) became much lower than that of the raw pulp (5.09 nm). The diffracted intensity indicating 101 crystal planes nearly disappeared from the XRD curve of AHIMCl treated pulp samples. The X-ray photoelectron spectroscopy (XPS) analysis indicated that the significant reduction in C_{1s2} and O_{1s2} contents of the regenerated samples after the AHIMCl treatment implies that AHIMCl severely destroy the hydrogen bonds in crystalline and amorphous regions.

Keywords: Degradation; Treatments; Pulp; Ionic liquid

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INTRODUCTION

Treatments for lignocelluloses have attracted great attention in recent years because of their potential to achieve new interesting properties (Dawson 1997; Farrell *et al.* 2006; Hahn-Hägerdal *et al.* 2006). The approaches for treatment including physicochemical methods, combined with biological or mechanical processes, have been universally used in the production of biodegradable plastics, paper, biofuels, and biocompatible composites (Cowling *et al.* 1976; Lynd *et al*. 1991; Sun *et al*. 2002; Pérez *et al*. 2002; Zhang *et al*. 2007; Liu *et al*. 2008; Pérez *et al.* 2010). For example, alkali liquors (*e.g*., NaOH and KOH) and amine-based compound solutions (*e.g*., ethanediamine and liquid ammonia) have been widely used for the treatments of lignocelluloses, making the application of bio-based resources in other industries possible (Ouajai *et al*. 2005; Orden *et al*. 2006; Pérez *et al*. 2010; Wang *et al*. 2010; Wan *et al*. 2011). In these processes, chemical and physical structures indicating the surface or/and interior of lignocelluloses are changed as a result of the conditions of treatment, and such changes have been used as the necessary base for the further applications.

Current studies for treating lignocelluloses, such as alkali liquor treatments, have been mostly performed in a heterogeneous phase (Mannan 1993; Oh *et al*. 2005; Ouajai *et al*. 2005; Urreaga *et al*. 2007; Wan *et al*. 2011; Heinze *et al*. 2001). In most heterogeneous systems, however, these approaches cause various problems such as non-uniform reactions, lower efficiency, and heavy pollution. In this regard, homogeneous systems offer the potential not only to overcome these problems, but also to contribute innovation for treating lignocelluloses. For example, green ionic liquids (ILs) (*e.g*., 1-Butyl-3-Methylimidazolium Chloride (BMIMCl) and 1-Allyl-3-methylimidazolium Chloride (AMIMCl)) have been recently developed, making it possible to treat celluloses in a homogeneous phase due to their perfect dissolution of lignocelluloses (Kantelinen *et al*. 1993; Fink *et al*. 2001; Ren *et al*. 2003; Cao *et al*. 2009; Lee *et al*. 2009). Treatments achieved in homogeneous phase may contribute to a complete and uniform change relative to both the surface and crystalline structure, an effect that is nearly impossible to achieve when employing heterogeneous phases. However, information on these distinctions in heterogeneous and homogeneous phases is rather scarce in the literature.

Pretreatments are widely regarded as an essential step in processing of lignocelluloses, rendering the material suitable for further processing in the production of biofuels, chemicals, and so on. This paper aims at providing a theoretical basis for pretreatments of lignocelluloses in the two different phases. In this work, Bleached Kraft Softwood Pulp (BKSP) was used as the lignocellulosic material. Heterogeneous NaOH and EDA solutions and homogeneous 1-Allyl-3-Hexylimidazolium Chloride (AHIMCl) treatments for lignocelluloses were investigated and compared. The effects of these treatments on the mean degree of polymerization, crystalline structure, and thermal stability of the pulp samples were investigated and compared by X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Thermogravimetric (TG), and Scanning Electron Microscope (SEM) analyses.

EXPERIMENTAL

Materials

Bleached Kraft Softwood Pulp (Wood species, *Pinus massoniana*) was supplied by Guangdong Eagle Force Paper Co., Ltd (Guangdong, China). Copper (II)-ethylene-diamine complex (CED) was supplied by J&K Scientific Co., Ltd (Beijing, China). The ethylenediamine-to-copper ratio in the CED solution was 2.00±0.04 to 1, with copper molarity of 1.00±0.02 mole. Chemical agents including sodium hydroxide (NaOH) and EDA were purchased from Guangzhou Qianhui Bose Instrument Co., Ltd (Guangdong, China). 1-Allyl-3-Hexylimidazolium chloride ionic liquid (AHIMCl) (Chemical formula, $C_{12}H_{21}N_2Cl$) was synthesized in accordance with the method of Liu *et al*. (2012): To N-Hexylimidazole in a glass-lined reactor, approximately 1:1.2 molar ratio of allyl chloride was added dropwise under argon gas atmosphere at room temperature. After completely adding the allyl chloride, the reaction mixture was stirred magnetically with reflux at 55 °C for about 10 h. After removing the residual allyl chloride under reduced pressure, the resulting liquid was repeatedly washed with an excess amount of ether to eliminate the residual N-hexylimidazole. The resulting IL solution was dried under vacuum at 80 °C for 72 h.

Methods

Pretreatment of the BKSP

The BKSP of *Pinus massoniana* species with weight-average length of 1 to 3 mm and weight-average width of 26 to 28 μm, was dispersed after being soaked in water for 24 h. Subsequently, the BKSP slurry was treated with 0 to 20 wt% aqueous NaOH and 20 wt% EDA solutions at 5 °C for 72 h. The pretreatment of the raw BKSP with AHIMCl was conducted as follows: In 5 mL of AHIMCl, approximately 8% of the raw BKSP was added and subsequently stirred by magnetic method at 100 °C until complete dissolution. After the pretreatments, the BKSP slurry was washed with deionized water until the pH of the washings was 7. After filtration, the treated samples were dried under vacuum at 40 °C for 24 h. The reason for placing the regenerated cellulose samples in water matter is that new hydrogen bonds between cellulose chains are restructured by water molecular after the cellulose solution is inserted into the water phase. In this process, anions and cations from ILs located between hydrogen bonds of cellulose chains are replaced by H^+ and OH^- from water molecular (Liu *et al.* 2012).

Mean degree of polymerizations analysis

The mean degree of polymerizations of the BKSP treated with aqueous NaOH and EDA solution with concentration from 1% to 20 wt% at 5 to 80 ^{o}C, were investigated by the viscosity method (GB, 1986).

Degree of crystallinity analysis

The XRD method serves as the most widely used method to investigate the crystal structures of lignocelluloses (Park *et al*. 2010). The crystal structures of the BKSP treated with aqueous 20 wt% NaOH and EDA solutions at 5 ^{o}C, as well as AHIMCl, was analyzed using an XRD analyzer (Rigaku D/max-III X-ray diffractometer) set at 40 kV and 30 mA. Wide-angle x-ray intensities were collected for 2θ values ranging from 4° to 60°, with a step scanning rate of 8°/min and step increment of 0.04°.

The degree of crystallinity is calculated by the following equation (Segal *et al.* 1959),

$$X_c = {\left(I_c - I_{(am)}\right)\times 100} \Big/ {I_c} \tag{1}$$

where X_c indicates the crystallinity of BKSP sample; I_{am} is the intensity of amorphous regions of Cellulose I and Cellulose II at diffraction angle of 15.0°and 18.0°, respectively; and I_c is the intensity of crystal planes of Cellulose I and Cellulose II, respectively.

Crystallite size analysis

The crystallite size of BKSP sample was calculated by the Scherrer formula (Cao *et al*. 2002),

$$D = {K\lambda}/{\beta \cos\theta} \quad (2)$$

where K is the Scherrer constant (0.89), D is the apparent crystallite size (nm), λ is the wavelength of the X-ray (0.154056 nm), β is the full width at half maximum (rad), and θ is the diffraction angle.

TGA analysis

Thermogravimetric analysis (TGA) was used to study the thermal stability of the BKSP treated with aqueous 20 wt% NaOH and EDA solutions, as well as AHIMCl. A TGA Q500 instrument was used to record weight loss within the range of room temperature to 500 ^{o}C, with a heating rate of 10 ^{o}C/min. The test samples for TGA were fibrous solids of about 25 mg. The flow rate of nitrogen source was 25 mL/min. The TGA pan was made of platinum.

XPS analysis

X-ray photoelectron spectroscopy (XPS) analysis was conducted to study the effects of treatments on the main elements (*e.g.*, C and O) on the BKSP. The surface of samples was observed using a Kratos AXis Ultra DLD (Kratos Company, Britain) at 7.9×10^{-10} vacuum degree by Mono (Al) source. Energy resolution was 0.48 eV, and the spatial resolution imaging was 3 μm. And the spatial resolution was 95 nm.

SEM analysis

A scanning electron microscope (SEM) was used to examine the surface image of the raw BKSP samples and AHIMCl-treated BKSP samples. All the samples were fixed to a metal-base specimen holder using double-sided, sticky tape. The fixed samples were coated with gold, and they were then observed using a Philips XL-30 ESEM scanning electron microscope.

RESULTS AND DISUSSION

Effects of Treatments on the Mean Degree of Polymerization

The mercerized cellulose can be obtained by a treatment using a certain concentration of aqueous NaOH solution (Kolpak *et al*. 1978). In this process, aqueous NaOH solution swells and mercerizes the cellulose, changing the crystalline structures from cellulose I to cellulose II (Francis *et al.* 1978).

Figure 1 shows the effects of the different concentrations of aqueous NaOH solution on the mean degree of polymerization of the BKSP. By increasing the concentration of aqueous NaOH solution from 1 wt% to 20 wt%, the mean degree of polymerization of the BKSP exhibited initially a decrease and subsequently an increasing tendency. When the raw BKSP was treated with lower concentrations of aqueous NaOH solution (≤5 wt%), the mean degree of polymerization slightly decreased because of cleavage of some of the glycosidic linkages in cellulose molecules from alkali degradation.

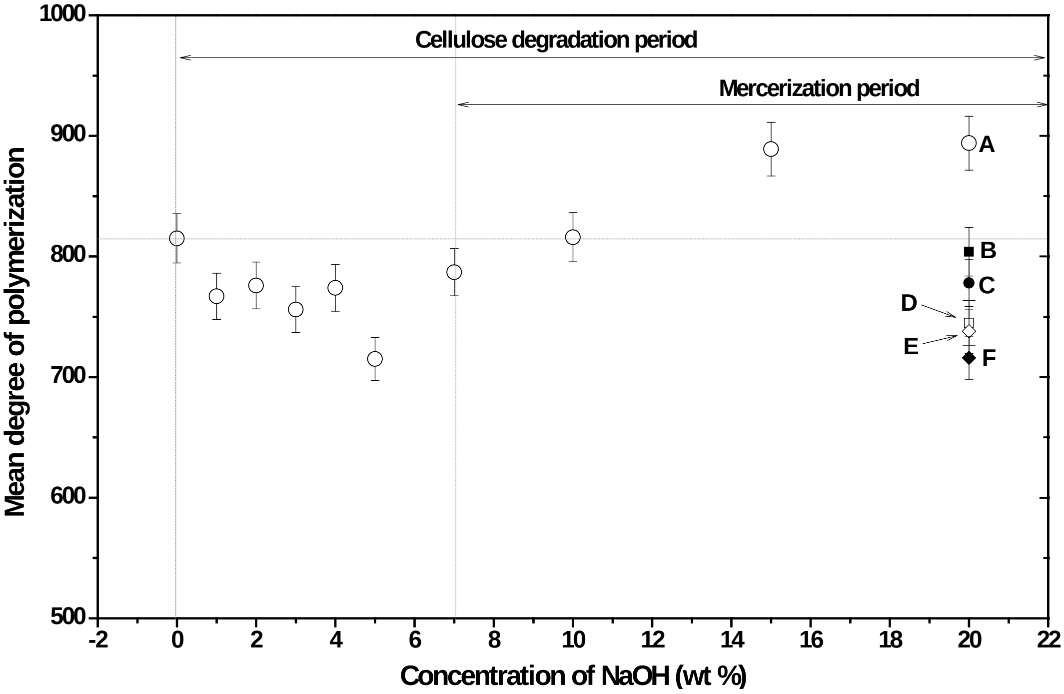

Fig. 1. Mean degree of polymerization as a result of the concentration and temperature of treatments of the raw BKSP by NaOH and EDA solutions. A = Mean degree of polymerization of the BKSP treated by 0 to 20 wt% NaOH solution at room temperature for 4 h; B = Mean degree of polymerization of the BKSP treated by 20 wt% EDA solution at room temperature for 72 h; C = Mean degree of polymerization of the BKSP treated by 20 wt% NaOH solution at 50 ºC for 4 h; D = Mean degree of polymerization of the BKSP treated by 20 wt% NaOH solution at room temperature for 72 h; E = Mean degree of polymerization of the BKSP treated by 20 wt% NaOH solution at 5 ºC for 72 h; F = Mean degree of polymerization of the BKSP treated by 20 wt% NaOH solution at 80 ºC for 4 h.

As the concentration of aqueous NaOH solution was further increased to 20 wt%, the mean degree of polymerization of the BKSP increased. Moreover, the mean degree of polymerization of the BKSP samples treated with 15 wt% and 20 wt% aqueous NaOH solutions was greater than that of the raw BKSP. Small polyose derivatives resulting from the aqueous NaOH solution with higher concentrations are probably reaggregated in the process of water for washing at 5 ^{o}C. This contributes to an increase of viscosity of the cellulose solution in CED solvent. Viscosity of cellulose solution is used to estimate the mean degree of polymerizations of cellulose samples. With the treatment of 20 wt% NaOH solution, however, the mean degree of polymerization of the BKSP samples decreased significantly with the increase in treating temperature or time (See Fig. 1). Instead of polymerization, severe alkaline degradation occurred at high temperatures (e.g., 80 °C). Compared with the 20 wt% NaOH solution treatment, the 20 wt% EDA solution treatment had lesser effect on the mean degree of polymerization of the BKSP.

Crystalline Structure of the Treated BKSP

Treatments may influence not only the mean degree of polymerization, but also the crystal structures of the BKSP samples. In the present study, the aqueous NaOH and

EDA solutions exhibited chemical effects on the cellulose structure partly because of the cleavage of cellulose chains by alkaline reaction. However, a previous study reported that the ILs investigated displayed mainly physical effects on cellulose structure by breaking the hydrogen bonds between cellulose chains (Pinkert *et al*. 2009). Figure 2 illustrates the effects of the aforementioned treatments on the crystal structures of the BKSP samples.

After the aqueous NaOH and AHIMCl solution treatments, the crystal form of cellulose I of the raw BKSP had been transformed to cellulose II. The distinct diffracted intensity of the above BKSP samples at 2θ values was less intense. Moreover, the intensity shifted to a lower 2θ value of 21.20° after the 20 wt% aqueous NaOH solution treatment at 5 ^{o}C. A more distinct decrease in diffracted intensity was observed after the AHIMCl treatment; the weak diffracted intensity of the BKSP samples treated with AHIMCl at 2θ values shifted to a lower 2θ value of 21.72°. Under this condition, the diffracted intensity indicating 101 crystal plane nearly disappeared (as shown in Fig. 2). The crystalline structure of the BKSP was damaged by ILs (Miyafuji *et al*. 2009).

As shown in Fig. 3, the aforementioned treatments damaged the crystal structure of cellulose. The degree of crystallization of raw BKSP decreased from 63.93% to 61.35% and 52.96% after the 20% aqueous NaOH and the AHIMCl treatments, respectively. However, after the 20% aqueous EDA solution treatment the degree of crystallization of raw BKSP decreased to approximately 40.5%. This result suggests that EDA has a special decrystallization effect on lignocelluloses (Nada *et al.* 1990).

The 002 crystal plane size of the BKSP samples varied almost in the same manner during the aforementioned treatments. After the AHIMCl and EDA solution treatments, the 002 crystal plane size of the BKSP samples (1 nm) became lower than that of the raw BKSP (5.09 nm). This result shows that, unlike the aqueous NaOH treatment, the EDA solution and AHIMCl treatments can severely damage the crystalline structure of lignocelluloses.

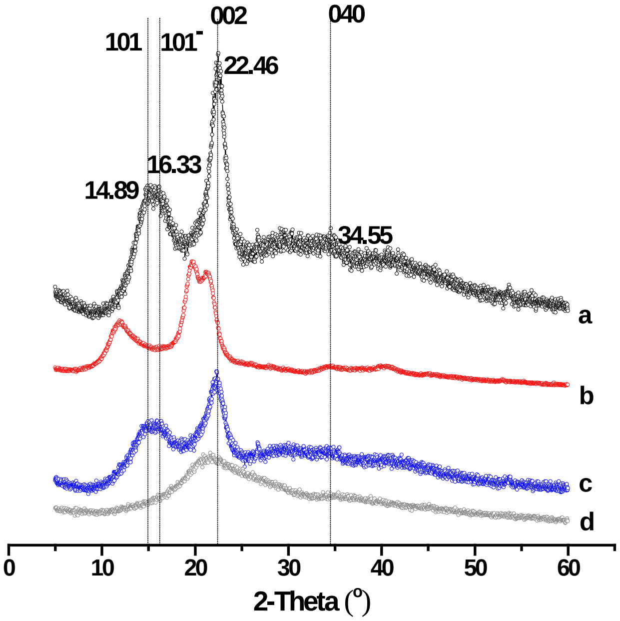

Fig. 2. XRD patterns of the raw BKSP (a), 20 wt% NaOH-treated BKSP samples (b), 20 wt% EDA-treated BKSP samples (c) for 72 h at 5 ºC, and AHIMCl-treated BKSP samples (d)

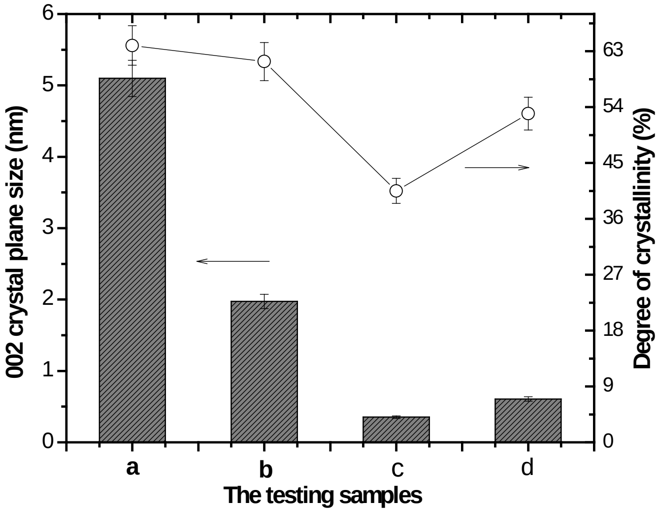

Fig. 3. 002 crystal plane size and degree of crystallinity of the BKSP samples (a) resulting from 20 wt% NaOH (b) and EDA (c) treatments for 72 h at 5 ºC, and AHIMCl (d) treatments.

Electron Spectroscopy for Chemical Analysis

X-ray photoelectron spectroscopy (XPS) analysis was performed to investigate in detail the EDA solution and AHIMCl-treated BKSP samples. As shown in Fig. 4, the main elements (*i.e.*, C and O) were observed on the surface of the BKSP samples after the treatments. In addition, the N and Cl elements were observed on the surface of the BKSP samples treated with AHIMCl. These observations indicate that a small amount of AHIMCl residue was retained on the surface of the BKSP despite abundant washings by water.

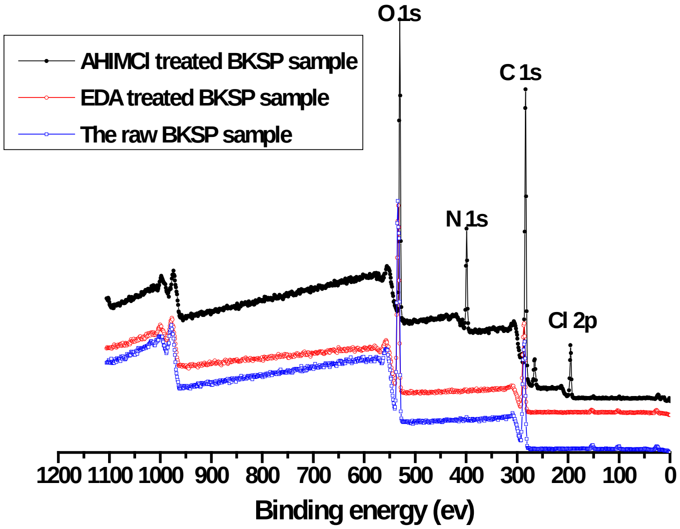

Fig. 4. XPS wide scan spectra of the raw BKSP and the BKSP samples treated by AHIMCl and 20 wt% EDA, respectively.

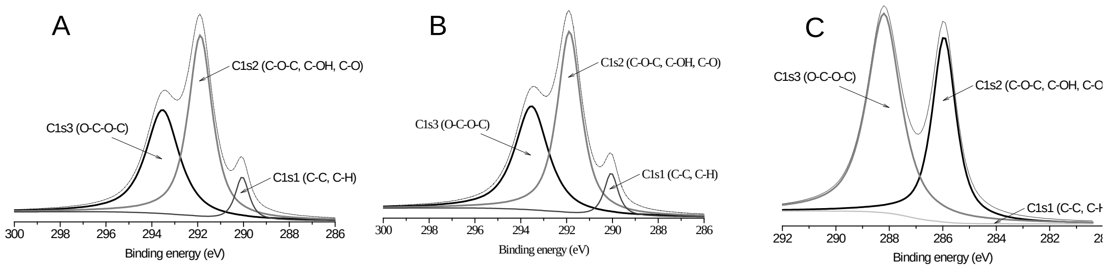

Fig. 5. XPS spectra of C_{1s} of the raw BKSP (A), EDA-treated BKSP (B), and AHIMCl-treated BKSP (C) samples

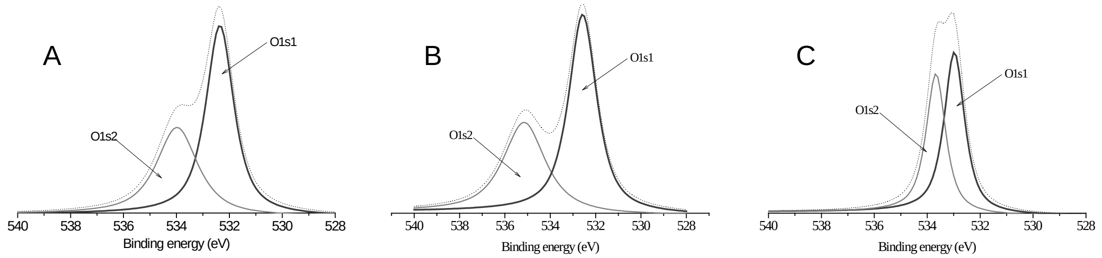

Fig. 6. XPS spectra of O_{1s} of the raw BKSP (A), EDA-treated (B), and AHIMCl-treated BKSP samples (C) samples

Peak deconvolution was applied to investigate the spectra of C_{1s} and O_{1s} peaks to determine the changes in the chemical elements and bonds information after the treatments. The peaks resulted in three carbon (C_{1s1}, C_{1s2}, and C_{1s3}) and two oxygen (O_{1s1} and O_{1s2}) components. A previous study reported that the binding energy of C_{1s1}, C_{1s2}, and C_{1s3} is 285.0 eV, 286.8 eV, and 288.0 eV, respectively, in the cellulosic solid phase (Gelius *et al*. 1970). C_{1s1} indicates the carbon element linked to hydrogen or to carbon (-C-H or -C-C). C_{1s2} shows carbon element linked to a single oxygen element (-C-O-), whereas C_{1s3} bonds to two non-carbonyl oxygen atoms [-C (O)-O-] or a single carbonyl oxygen atom (-C=O) (Dorris *et al*. 1978a,b). Remarkable differences in the relative contents of C_{1s1}, C_{1s2}, and C_{1s3} components were observed after the treatments (as shown in Fig. 5). As shown in Table 1, the binding energy of C_{1s1}, C_{1s2}, and C_{1s3} was 284.56 eV, 286.38 eV, and 288.03 eV, respectively. These results are consistent with those reported in the literature (Dawson, 1997; Hua *et al*. 1993a; Hua *et al*. 1993b; Jaić *et al*. 1996; Wistara *et al*. 1999). The XPS spectrum of the BKSP samples treated with EDA solution and AHIMCl was dominated by the C_{1s1} peak (C-C and C-H bonds) with a relatively low peak width of 1.50 eV.

Previous studies suggested that C_{1s1} mainly implies the content of lignin and extractives, because carbohydrates give rise only to C_{1s2} and C_{1s3} peaks (Ahmed *et al*. 1987; Kamdem *et al*. 1991). The relative C_{1s1}, C_{1s2}, and C_{1s3} contents of the raw BKSP samples were 7.13 %, 51.84 %, and 41.03 %, respectively (as shown in Table 1). The data imply that the BKSP contains only marginal lignin and mostly cellulose and hemicellulose (Dorris *et al.* 1978a; Hua *et al.* 1993a).

Table 1. C_{1s} XPS Data for the BKSP Samples

Sample	*E* (*ev*)			Relative content (*%*)		
	C_{1s1}	C_{1s2}	C_{1s3}	C_{1s1}	C_{1s2}	C_{1s3}
The raw BKSP	284.56	286.38	288.03	7.13	51.84	41.03
EDA treated BKSP	284.13	285.90	287.26	6.17	64.64	29.19
AHIMCl treated BKSP	284.27	286.19	287.43	0.01	39.64	60.35

Compared with the raw BKSP, the BKSP samples treated with EDA had more C_{1s2} and less C_{1s1} content, whereas that treated with AHIMCl had less C_{1s1} and C_{1s2} contents but more C_{1s3} content (as shown in Table 1). The decrease in the relative C_{1s1} content shows that the carbohydrate on the surface of the BKSP increased after the EDA solution and AHIMCl treatments. This contribution of C_{1s2} to C-O bonding indicates that there were changes in the hydrogen bonds in the cellulose region. Thus, the AHIMCl treatment can severely destroy the abundant hydrogen bonds in cellulose regions. This conclusion can be explained by the fact that the cation [$AHIM^+$] and anion [Cl^-] from AHIMCl attack the hydrogen bonding in crystalline and amorphous regions (Pinkert *et al*. 2009). However, the C_{1s2} of the BKSP samples treated with EDA solution tended to be higher, which might have resulted from the reconstruction of hydrogen bonding.

The C-O bonding in lignocelluloses mainly consists of C-OH-O and free C-OH, which can be expressed by O_{1s1} and O_{1s2} XPS peaks, respectively (Hua *et al*. 1993b). Therefore, the relative O_{1s1} content mainly reflects the changes in hydrogen bonds between oxygen elements and hydroxyl groups, whereas O_{1s2} exists only in hydroxyl groups (Ahmed *et al*. 1987a,b). The O_{1s1} and O_{1s2} XPS peaks of the above treating samples are also shown in Fig. 6. The O_{1s1} and O_{1s2} binding energies of the raw BKSP were 532.36 and 533.98 eV, respectively (see Table 2).

Table 2. O_{1s} XPS Data of the BKSP Samples

Sample	*E* (ev)		Relative content (%)	
	O_{1s1}	O_{1s2}	O_{1s1}	O_{1s2}
The raw BKSP	532.36	533.98	59.85	40.15
EDA treated BKSP	532.57	535.15	60.06	39.94
AHIMCl treated BKSP	532.97	533.67	55.19	44.81

These results agree well with those previously reported (Dorris *et al*. 1978a,b; Ahmed *et al*. 1978a,b). After the AHIMCl treatment, the O_{1s1} of the BKSP samples decreased by 4.66%. This result indicates that the hydrogen bonds in the BKSP samples were destroyed by AHIMCl, an effect that was also observed in the C_{1s} XPS peak discussed above. The high O_{1s1} content observed is probably the result of the reconstruction of hydrogen bonding during washing of the BKSP/AHIMCl liquid with water. After the EDA solution treatment, the O_{1s1} content slightly increased.

Thermal Stability

The chemical treatments probably contribute to the changes in the thermal stabilities of the BKSP samples. Figure 7 shows the TGA curves of the raw BKSP and the BKSP samples treated with aqueous NaOH and EDA solutions, as well as with AHIMCl. From room temperature to 150 ^{o}C, the weight losses of the BKSP samples after aqueous 20 wt% NaOH, EDA solutions, and the AHIMCl treatments were 3.01%, 3.67%, and 11.63%, respectively. The weight losses of the BKSP samples after AHIMCl treatment were higher than those of the other samples.

As shown in Fig. 7, the greatest decomposition of the AHIMCl-treated BKSP samples occurred at 255.1 °C (T_d), which was lower than that of EDA- (345.9 °C) and NaOH-treated (346.1 °C) BKSP samples. The combined weight loss of the AHIMCl-, EDA-, and NaOH-treated BKSP samples at 150 °C to T_d was 41.42%, 55.77%, and 57.13%, respectively (as shown in Fig. 7).

Based on the similar combined weight loss and highest decomposition temperature of the BKSP samples, commercial EDA and NaOH solutions did not have a signifycant effect on thermal stabilities of the BKSP samples. This finding indicates that nearly all the damage in the crystalline structure and the structural rearrangements of cellulose chains results from the dissolution of the BKSP in AHIMCl (Muhammad *et al*. 2010).

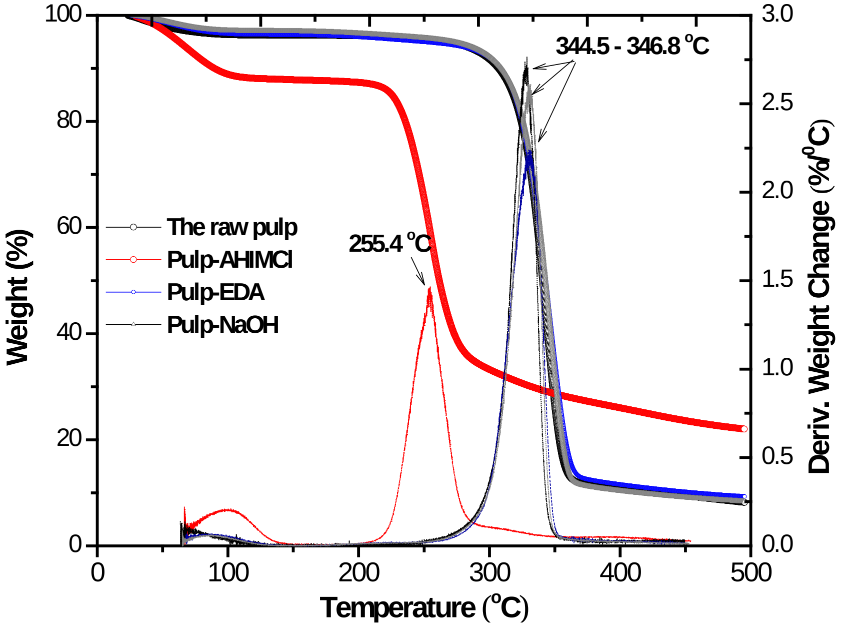

Fig. 7. Temperature dependencies of weight loss for the BKSP samples by the treatments of aqueous NaOH and EDA solutions, as well as with AHIMCl

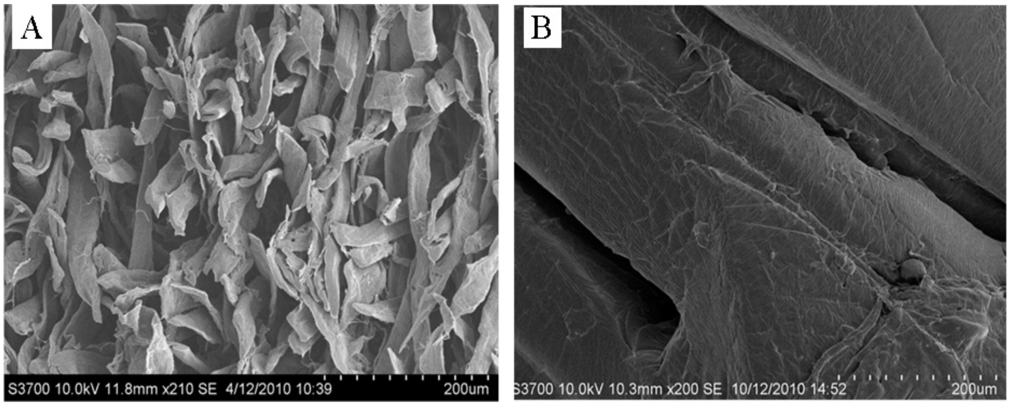

Fig. 8. SEM image of raw BKSP (A) and the regenerated samples treated by AHIMCl (B) (×200)

The results showed that the BKSP samples after the treatments by 20 wt% NaOH and EDA solutions still retained nearly the same morphology in heterogeneous phases. No single fiber from the BKSP samples was observed, however, after the treatments with AHIMCl, due to the dissolution in a homogeneous phase. As shown in the SEM images, the regenerated samples treated with AHIMCl exhibited an unordered rearrangement of cellulose chains that was in contrast to the raw BKSP samples, which consisted of glossy arrangements of the BKSP fibers (See Fig. 8).

CONCLUSIONS

1. Increasing the treating temperature or time decreased the mean degree of polymerization of the BKSP in the 20 wt% aqueous NaOH solution.
2. An increased mean degree of polymerization of the BKSP was observed when increasing the concentration of aqueous NaOH solution from 5 wt% to 20 wt%.
3. 20 wt% EDA solution treatment had a negligible effect on the mean degree of polymerization of the BKSP, but it had a great effect on the degree of crystallization and the 002 crystal plane sizes of the BKSP samples.
4. After the AHIMCl treatment, the degree of crystallization and 002 crystal plane sizes of the BKSP samples decreased significantly, and resulted in poor thermal stability.
5. Compared with the raw BKSP, the EDA-treated BKSP had more C_{1s2} and less C_{1s1} content, whereas the AHIMCl-treated BKSP samples had less C_{1s1} and C_{1s2} content. The reduction in C_{1s2} and O_{1s2} contents of the AHIMCl-treated BKSP samples indicates that AHIMCl can destroy hydrogen bonds.

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