Inhibition of Hornification of Eucalyptus Kraft Pulp by Acetylation

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Abstract. Bleached eucalyptus Kraft pulp was acetylated with acetic anhydride under mild conditions, and recycling treatments were performed for acetylated pulp and unmodified pulp. The results indicated that Kraft pulp could be acetylated with acetic anhydride in absence of the catalyst, and hydrophobic acetyl functional groups were introduced into cellulosic fibres. Acetylation can restored the swelling ability of Kraft fibres, inhibit the hornification of Kraft pulp and improve pulp performance with the progress of cycles.

1. Introduction

Recycled pulp is the main raw materials for the production of newsprint, wrapping paper and linerboard in papermaking industry. However, the quality of recycled pulp decreases with the growing number of cycles, (Yamauchi et.al 2008). It has been suggested that decrease in the quality of recycled pulp is caused by the hornification effects, the irreversible closure of pores in cell walls and the loss of swelling capacity (Fernandes et al. 2004). Chemical modification is a way to reduce fiber hornification effects; Acetylation is commonly used for the production of cellulose acetate, the cellulose is first swelled in acetic acid and then acetylated with acetic anhydride in the presence of sulfuric acid as catalysts (Fischer et al. 2008).

The present work used eucalyptus Kraft pulp as a sample which was acetylated by acetic anhydride without adding catalyst; this work attempted to introduce hydrophobic acetyl functional groups into cellulosic fibers, inhibit fiber hornification effects by acetyl functional groups, and improve the quality of recycled pulp.

2. Experimental

2.1. Raw materials

Never-dried Bleached Eucalyptus Kraft Pulp was kindly provided by Dingfeng Paper Mill (Guangdong, China), the beating degree was 45^0SR. Chemicals (i.e., acetic anhydride, HCl, NaOH) were of analytical grade.

2.2. Pulp preparation and acetylation

The pulp samples were disintegrated according to ISO 5263 (2005), then acetylation was performed with two steps, (1) acetic anhydride hydrolysis: 20g of pulp sample and 170ml of acetic anhydride were

placed inside sealable plastic bags, and kept at the temperature of 60^0C for 1h in water bath. (2) Pulp acetylation: the excess amount of reaction solution was removed, and 100ml of acetic anhydride was added to carry out the acetylation reaction at a consistency of 10% at 80^0C for 1h. Finally, the pulp sample was thoroughly washed to remove residual traces of acetic acid and acetic anhydrides. The unmodified pulp sample was prepared as described above without addition of acetic anhydride.

2.3. Determination of degree of substitution (DS)

Substitution degree of acetylation of the pulp sample was determined as Equation 1 according to ASTM D871-72. (1983).

$$[(D-C)N_{HCl}+(A-B)N_{NaOH}]\times\frac{6.005}{W}=\frac{6000X}{162+42X} \quad (1)$$

Where A is the volume of NaOH used for pulp sample (ml); B is the volume NaOH used for blank sample (ml); C is the volume of HCl used pulp sample (ml); D is the volume of HCl used for blank sample (ml); N_{HCl} is the consistency of HCl solution (M); N_{NaOH} is the consistency of NaOH solution (M); X is substitution degree (%); W is dry weight of pulp sample (g).

2.4. Water retention value (WRV)

The centrifugal machine (BY-G10, Baiyang Medical Instrument Co., Ltd, Beijing, China) was used for WRV analysis of pulp samples according to ISO 23714 (2007) (3000g, 15min). WRV was calculated from Equation 2.

$$W=(W_1-W_2)/W_2 \quad (2)$$

Where W_1 is the weight of pulp after centrifugation (g), W_2 is the weight of the absolute dry pulp samples (g).

2.5. FTIR analysis

The Infrared spectra of pulp samples were characterized by the Fourier Transform Infrared Spectrometer (FTIR, Tensor 27 Bruker). FTIR samples were prepared with KBr disc method. All spectra were scanned in the range of 4000 to 400cm^{-1} with a total of 32 scans at a resolution of 4cm^{-1}.

2.6. XRD Characterization

The crystallinity of pulp samples was determined by X-Ray Diffractometer with Cu-Kα radiation (Bruker, Germany). XRD measurements were performed with a scan step size of 0.013 (2θ), and the time per step of 15s, the scattered radiation was detected in the angular range from 10-40^0 (2θ), crystallinity (X_c) was calculated as Eq.3 according to (Park et al. 2010).

$$X_c=A_{cr}/(A_{cr}+A_{am}) \quad (3)$$

Where A_{cr} is area of crystalline phase, A_{am} is area of amorphous phase.

2.7. Pulp recycling and strength test

Handsheets were prepared with a basis weight of 70g/m2 according to ISO 5269 (2005). The handsheets were dried in vacuum oven at 1050C for 6hrs, and then soaked in de-ionized water for 24 hours before disintegration for making the handsheets of the second cycles. The recycling treatment was repeated three cycles. R_0, R_1, R_2 and R_3 represented the pulp samples subjected to 0, 1, 2 and 3 cycles respectively. The tensile strength and internal bond strength (IBS) of handsheets were measured according to ISO 5269 (2009).

3. Results and Discussion

3.1. Pulp acetylation

The purpose of acetylation was to introduce acetyl groups to microfibrils surface. DS of modified cellulose should be lower; otherwise the bonding ability of fibers would be lost because of hydrophobic acetyl groups substituting hydrophilic hydroxyl groups. The result indicates that DS of acetylated pulp was 0.145, well below that of common form of cellulose acetate ranging from 2 to 2.5 (Fischer et al. 2008). Lower DS might be due to the absence of catalyst.

3.2. FTIR analysis

The acetylation of pulp was clearly confirmed by the characteristic peaks of FTIR spectra, as shown in Figure 1. In contrast to the unmodified pulp spectrum, there were some new peaks in the acetylated pulp spectrum, namely the symmetric stretching of C=O of the acetyl group (CH3C (O) O-) at 1730 cm^{-1}, the C-H bonds in methyl group (-CH3) at 1373cm^{-1}, and the vibrations of C-O in acetyl groups at 1248 cm^{-1}, and the peaks at 1640 cm^{-1} associated with the vibration of OH bonds in adsorbed water. Infar spectra of pulp samples demonstrated that it was successful to acetylate the pulp samples with acetic anhydrate.

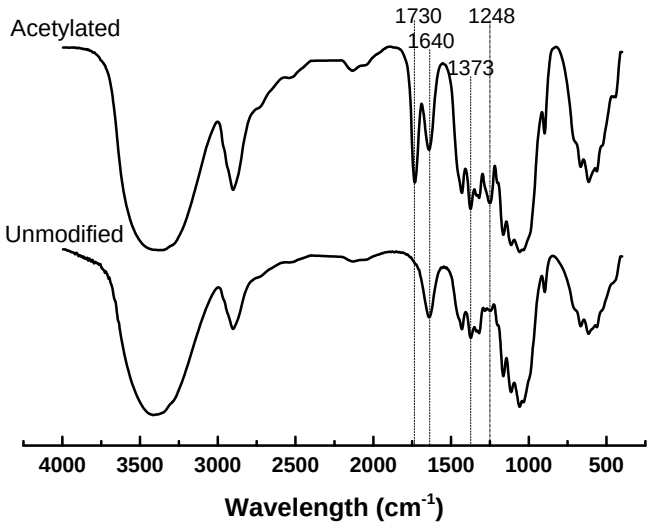

Figure 1. FTIR Spectra of unmodified pulp (bottom) and acetylated pulps (top)

3.3. XRD characterization

The impact of acetylation and recycling on crystallinity of pulp samples was evaluated by XRD characterization. The data of crystallinity of pulp samples are presented in table1. It can be found that crystallinity of both unmodified and acetylated pulps slightly increased with the growing number of recycling cycles, this result was in consistent with Somewang's report (Somewang et al. 2002). Crystallinity of pulp samples increased upon drying indicated the formation of hydrogen bonding between the surfaces of adjacent microfibrils in the amorphous region, and the partial amorphous regions were converted into crystalline regions.

Table 1. Crystallinity of the Pulp Samples with the Progress of Recycling

	R_0 (%)	R_1 (%)	R_2 (%)	R_3 (%)
Unmodified pulp	70.8	72.3	73.4	74
Modified pulp	67.2	69.7	71.2	72

It can also be seen from table1 that crystallinity of acetylated pulp was lower than that of unmodified pulp at the same number of cycles. This might be due to the introduction acetyl functional groups into the surface of microfibrils, which interfered with the formation of hydrogen bonding between adjacent microfibrils in the amorphous regions, and less amorphous regions in acetylated pulp were converted into crystalline regions compared to unmodified pulp, so that the crystallinity of acetylated pulp is lower than that of unmodified pulp.

3.4. WRV tests

WRV test is a common method to access the capability of water holding in fiber, the water include both water in the cell wall and also water associated with fiber surfaces (Hubbe et al. 2007).

The impacts of progress recycling on WRV of pulp samples can be assessed on table 2; it can be found that WRV of both unmodified pulp and acetylated pulp decreased noticeably with the growing number of cycles, and the largest decrease occurred after the first cycle. This was because an increase in crystallinity upon drying caused the irreversible closures of partial pores in cell walls resulting in a decrease in the swelling ability of fibers (Somewang et al. 2002). On the other hand, the WRV of the unmodified pulp and the acetylated pulp were 72.6% and 95% respectively after the third cycle. The higher WRV value of acetylated pulp was arisen from the introduction of acetyl groups, which interfered with the formation of hydrogen bonds in the amorphous region and reduced the crystallinity of the fiber, enhanced the re-opening ability of closed pores in the cell walls and improve the pulp WRV.

Table 2. WRV of pulp samples after given number of cycles.

	R_0 (%)	R_1 (%)	R_2 (%)	R_3 (%)
Unmodified pulp	146.3	90.7	80.4	72.6
Modified pulp	126.6	111.9	100	95

3.5. Sheet strength tests

The impacts of recycling and acetylation on pulp strength are illustrated as Figure 2. It can be seen that both tensile index and IBS of the unmodified pulp and acetylated pulp declined remarkably with repeated recycling. This was due to the generation of hydrogen bonding in amorphous regions of cellulose upon drying, part of amorphous regions was converted into crystalline regions, which led to parts of pores at cell walls were closed and the swelling ability of fibers deceased, the fibers became less conformability, and the tensile strength and IBS decreased. Tensile index and IBS of acetylated pulp were lower than those of unmodified pulp at R_0 cycle, which might be resulted from the hydrophobic acetyl groups located at the surface of microfibrils, which interfere with the formation of hydrogen bonding between microfibrils and a lower strength was generated

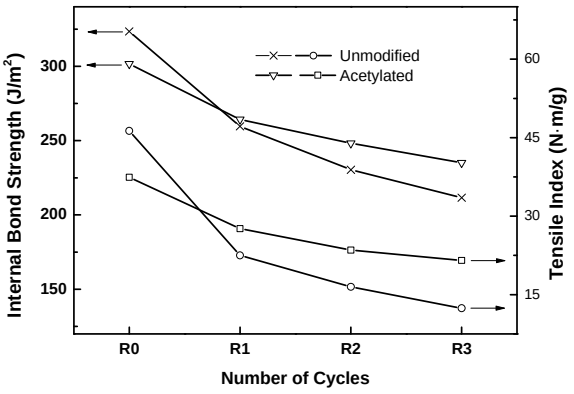

Figure 2. Strength of the pulp samples after given number of cycles

It can also be found that the strength of acetylated pulp was stronger than that of unmodified pulp after the first cycle, this might be that the introduced acetyl groups acting as a spacer hinder the formation of hydrogen bonds, less hydrogen bonds in amorphous regions resulted in a decrease in cellulose crystallinity, the swelling ability of fibers was improved, fibers became more conformable, which was beneficial to the relative bonding area of handsheets, thereby the strength of handsheets was increased.

4. Conclusion

FT-IR spectra indicated the successful acetylation of Kraft pulp with acetic anhydride at the absence a catalyst such as sulfuric acid, and acetyl functional groups were introduced into cellulose fibers.

Acetylation reduced the WRV and strength of Kraft pulp. However, acetylation could alleviate the decrease in cellulose crystallinity, improve swelling ability of Kraft pulp, prevent pulp from hornification, and improve the strength of Kraft pulp remarkably during the recycling process.

XRD characterization showed that bleached eucalyptus pulp displayed the typical X-ray diffraction pattern of cellulose I, and the diffraction pattern of acetylated pulp and recycled pulp remained unchanged, which revealed that either acetylation at mild condition or recycling did not change original crystalline structure of cellulose I.

Acknowledgments

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