

## Some Physical and Mechanical Properties of Uncatalysed Acetylated Paper

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The objective of this study was to investigate the influence of acetylation on properties of paper made using the chemi-mechanical pulp (CMP) process. Industrial unbleached CMP pulp was provided (before and after refining), and paper handsheets were made. After drying, the specimens were acetylated on a heated cylinder at 120 °C, with acetic anhydride without catalyst. Physical and mechanical properties including water absorption, porosity, printability, brightness, D-folding, breaking length, tear resistance, and burst strength of samples were measured and compared between treated samples and the controls. The results showed that acetylation intensity was increased by increasing reaction time. Water absorption exhibited a significant reduction due to acetylation. Brightness, D-folding, and burst showed an increasing trend as a function of the degree of acetylation. Tear resistance was decreased by acetylation. The refining process improved acetylation and decreased porosity. The results indicated that most of the important factors were significantly influenced and improved by both acetylation and the refining process.

*Keywords:* Acetylation; Refining; Physical properties; Mechanical properties; Paper; CMP process

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### INTRODUCTION

New processes are utilized to increase the quality, durability, and service life of forest products such as paper, which is a valuable resource. In this regard, improving the properties of these products in order to increase their efficiency is of particular importance. Wood and lignocellulosic materials have undesirable features such as moisture sensitivity. In fact, moisture affects the physical and mechanical properties of these materials. Also, dimensional changes with various amounts of moisture can occur in paper which will limit its effectiveness. Moisture sensitivity and swelling of the cell wall results in a lack of dimensional stability; this causes a reduction in mechanical properties and printability (Caulfield and Gunderson 1988).

It is assumed that hydrogen bonding between fibers plays a critical role in paper strength (Tiberg *et al.* 2001; Hubbe 2006). The hydroxyl groups (OH) are important reaction sites, and this bondability with water causes instability in the wood and lignocellulosic products (Matsuda 1996). Eliminating or inhibiting (blocking) these functional groups can avoid undesirable effects of hydrogen bonds in the materials and achieve better properties. One of the best ways to remove and deactivate these functional groups is by the replacement of these with stable chemicals. Chemical modifications have been applied to improve properties of wood and wood-based composites. Among the

various treatments, acetylation has been found to be the most effective and extensive application (Rowell 1998; Hill and Jones 1996). Acetylation involves esterification of the cell wall hydroxyl groups with or without catalyst. Acetylation is a single-site reaction that involves one acetyl group per reacted hydroxyl site with no polymerization (Rowell 2005). The effects of acetylation on tensile strength, tear, wet strength (Paulsson *et al.* 1998 cited by Abdulkhani *et al.* 2005), and photo-yellowing properties of unbleached and hydrogen peroxide bleached CMP pulp and paper have been studied (Abdolkhani *et al.* 2005). It was reported that mechanical properties of paper made by acetylated pulp are reduced, but properties in acetylated paper-sheets remain constant. Ebrahimzadeh (1998) studied the effect of acetylation on unbleached sulphate paper and found that acetylation reduced the amount of binding sites. Drakhshande *et al.* (2007) reported that acetylation of paper (bleached kraft long fiber) improves some of the physical properties such as water absorption. Acetylation of groundwood pulps improves their resistance towards light and, in some cases, also results in photo-bleaching of the pulp (Ek *et al.* 1992). Acetylation can also inactivate or remove some chromophores initially present in non-bleached pulp (Paulsson and Simonson 2002). Sain and Fotier (2002) studied refined and chemically modified Flax shives as a fiber resource for paper making. They reported that modification and refining improve moisture resistance and sheet formation. According to Nissan and Sternstein (1964), paper made from acetylated fibers tends to be bulkier with decreased strength. Acetylation decreases the water-holding ability of cellulose or hemicelluloses (Hubbe 2006), but the strength per unit of bonded area of acetylated fibers either remains constant or increases (Swanson 1956; McKenzie 1987).

Refining increased the inter-fiber bonding (Seth *et al.* 1979, cited by Hubbe 2006; Paulapuro and Thorp 1983), but the resulting internal delamination of individual fibers makes them less able to individually bear compressive loads (Hubbe 2006).

The objectives of this study were to determine the effects of acetylated treatment of paper (made using unbleached CMP pulp) on some mechanical and physical properties and to investigate the effects of refining on the acetylation process.

## EXPERIMENTAL

### Materials and Methods

Unbleached CMP pulp was obtained from the Mazandaran Wood and Paper Industry (MWPI) after and before refining. The species used in producing the pulp were hornbeam, beech, and birch with mixture percentages of 60, 20, and 20, respectively, and a Canadian standard freeness of 745 mL. Handsheets ( $60 \text{ g}\cdot\text{m}^{-2}$ ) were prepared according to TAPPI T 205 om-88 standard with a replication of five for treated paper and untreated. The paper sheets were then conditioned for 24 h at 23 °C and 50% RH, according to TAPPI standard before acetylation. The paper sheets were acetylated using technical grade acetic anhydride (without any catalyst). To obtain different degrees of acetylation, the conditioned handsheets were placed in a flask with an excess of acetic anhydride. The samples were then wrapped and placed at 120 °C for three different time periods (6, 8, and 11 h). The handsheets were then immersed in water to stop the acetylation reaction. The acetylated papers were then thoroughly washed with water to remove excess chemicals. The percentage figures specify the degree of acetylation according to the weight percent gain (WPG) due to reaction relative to the weight of the oven dry samples. Weight percentage gain (WPG) was calculated according to Eq. 1,

$$WPG (\%) = [(W_{act} - W_{unt}) / W_{unt}] \times 100 \quad (1)$$

where WPG indicates the weight percent gain (%); and  $W_{act}$  and  $W_{unt}$ , are oven dry weights after and before the acetylation (g), respectively.

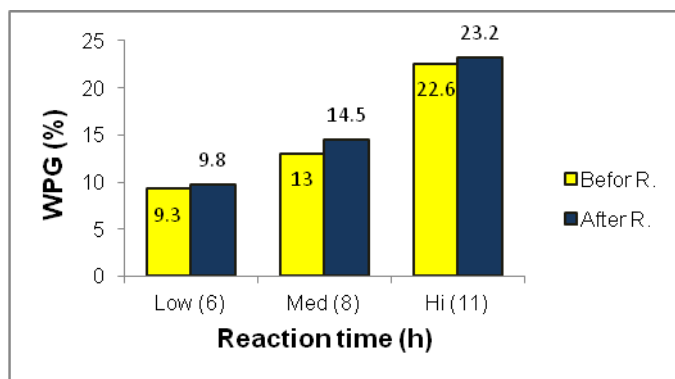
The variations were analyzed using PASW (SPSS, statistics processor, version 15) for Windows. The data were subjected to the one-way analysis of variance followed by Duncan's post-hoc.

Test procedures on water absorption (T 4441), porosity (T 547), smoothness (T 479), brightness (T 452), wax test (T 459 om-o3), breaking length (T 494 om-88), burst (T 403 om-91), tear (T 414 om88), and Double-Folding (D-folding) (T 495) were conducted, using the indicated TAPPI standard protocols.

## RESULTS AND DISCUSSION

### Weight Percent Gain

The Weight Percent Gain (WPG) due to acetylation was determined conventionally by weighing the samples before and after treatment. Results indicated that WPG was significantly increased in the course of processing and with increasing reaction time (Fig. 1). Based on the different reaction times, WPG can be divided into three intensities (low intensity for WPG between 8 to 10%, medium intensity for WPG between 13 to 15%, and high intensity for WPG between 22 to 24%) (Soltani *et al* 2008). Refining also increased WPG. It caused higher accessibility to OH groups than that of non-refined; thus substitution of acetyl groups was much faster than in non-treated samples, and this increased WPG.

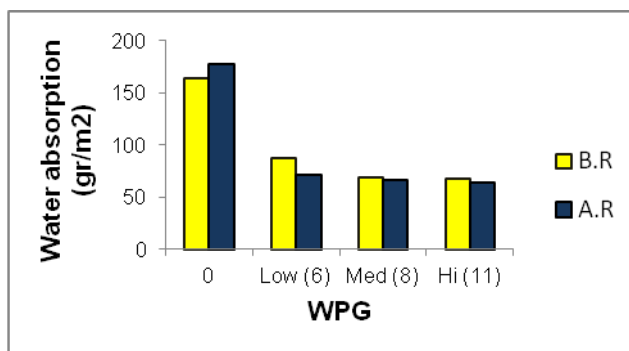


**Fig. 1.** Effect of reaction time of acetylation and refining process on weight percent gain (WPG)  
B. R= Before Refining; - A. R= After Refining

### Water Absorption

The water absorption in specimens with different treatment intensities are shown in Fig. 2. It was clear that water absorption decreased with acetylation. The values of water absorption were greater after the refining process compared to before refining. This was due to the higher accessibility of the hydroxyl functional groups, thereby increasing the bondability after the refining process (Matsuda 1996). Water absorption was increased in non-treated samples compared to non-refined samples (Fig. 1, WPG=0),

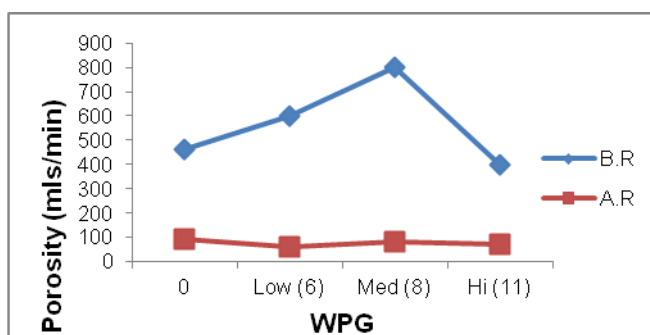
but after acetylation this accessibility caused a greater substitution of hydroxyl groups with acetyl groups and also a greater reduction in water absorption in the refined samples. This shows exactly where the substitution of hydrophobic groups (acetyl) by the hydrophilic groups (hydroxyl) will occur. These results are consistent with the findings of Drakhshande *et al.* (2007) and Sain and Fotier (2002).



**Fig. 2.** Effect of reaction time of acetylation and refining on water absorption of the CMP paper B. R= Before Refining; - A. R= After Refining

### Porosity

Figure 3 shows the effect of acetylation on porosity of the papers; results show there were no significant differences between treated and un-treated samples after refining (Fig. 3). Unlike the results of porosity before refining, the papers made from non-refined pulp showed significantly different values of porosity due to acetylation. Refining significantly decreased porosity compared to the non-refined materials.



**Fig. 3.** Effect of reaction time of acetylation and refining on porosity of CMP paper

### Brightness

Effects of acetylation and refining on the brightness of papers showed an increasing trend with increasing WPG (Fig. 4). This implies that acetylation had effects similar to a bleaching process. The effect may be related to the decrease in the hydroxyl content as a result of blocking by acetyl groups during acetylation. Similar results obtained by others suggest that some chromophoric groups are leached out by the acetylation (Abdolkhani *et al.* 2005; Paulsson and Simonson 2002).

Similar to water absorption, different behaviors were observed in refined and non-refined acetylated papers (Fig. 4). In non-acetylated papers, refining decreased brightness. On the other hand, refining increased brightness in acetylated papers. These

behaviors can be related to increasing light scattering due to delamination of the cell wall as a result of the refining process (Seth *et al.* 1979 cited by Hubbe 2006; Paulapuro and Thorp 1983).

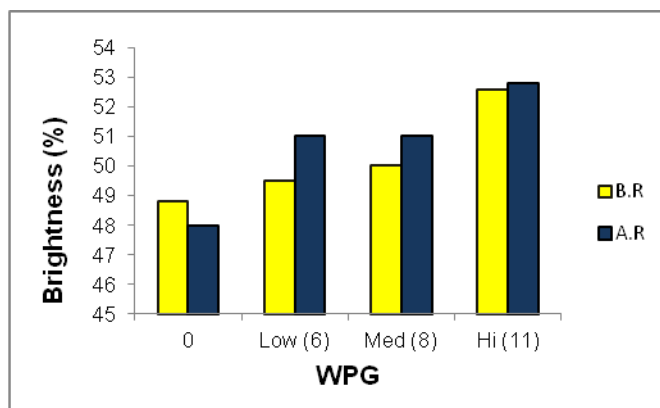


Fig. 4. Effect of reaction time and refining process on brightness

### Printability

Printability is an important factor that determines paper quality and can be measured with the wax test. As shown in Fig. 5, the effect of treatment on the wax number of non-refined paper was significant, and printability decreased due to acetylation; however after refining, the acetylation did not have a significant effect on the printability property. Printability is a function of bonding strength between fiber, the printing ink, and also surface quality. With increasing substitution of non-polar acetyl groups instead of polar hydroxyl groups, a reduction in polar functional groups can be observed in acetylated samples (Papadopoulos 2006), and this can be effective in reducing the bondability of the paper surfaces. On the other hand, acetylation increased roughness and may limit the interaction between printing ink and paper (Fardim 2002; Hubbe 2006). A decreasing trend in printability between refined and non-refined samples may be related to better surfaces quality of paper such as roughness after the refining process.

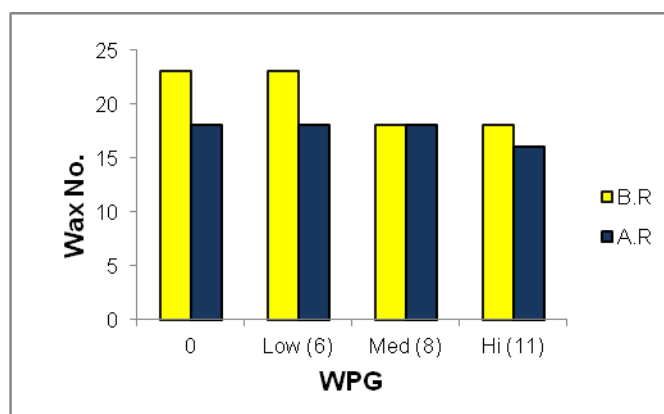


Fig. 5. Effect of reaction time of acetylation and refining on printability of CMP paper

## D-Folding

Results indicated that acetylation had a significant effect on the D-Folding of refined paper specimens (Fig. 6). D-Folding at low intensity of treatment (WPG=low) was decreased compared to those of control papers, but an increasing trend was observed with increasing intensity of acetylation. In non-refined papers, acetylation did not have a significant effect on the D-folding index. This implies that the refining process significantly affected and improved D-folding index. The reason for the improvement is possibly due to the increased inter-fiber bonding by the refining process (Paulapuro and Thorp 1983).

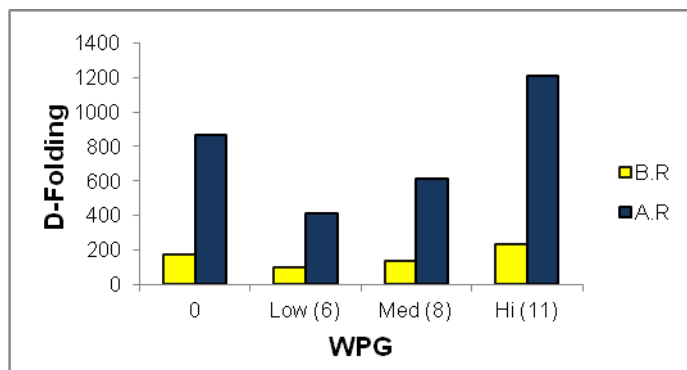


Fig. 6. Effect of reaction time of acetylation and refining on D-Folding of CMP paper

The D-Folding index is one of the most important properties of paper. A folding-endurance test is used to measure the ability of a paper to maintain its strength after repeated folding. Test results reflect the combined elastic and visco-elastic properties of the paper. Lack of folding endurance can result from lack of sufficient fiber length, inadequate fiber bonding, or brittleness (Caulfield and Gunderson 1988). Increasing D-folding index with increasing WPG of acetylation can be attributed to increasing strength per unit of bonded area of acetylated fibers (Swanson 1956; McKenzie 1987).

## Breaking Length

Breaking length is the calculated upper limit of the length of a uniform paper strip that would support its own weight when suspended at one end. The effect of acetylation on breaking length was not significant (Fig. 7).

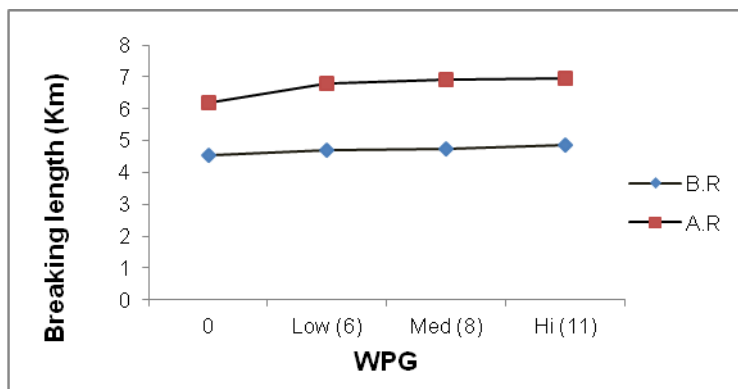


Fig. 7. Effect of reaction time of acetylation and refining on breaking length of CMP paper

However, breaking length was increased by refining. This was attributed to improved inter-fiber bonding due to refining.

### Tear Resistance

Tear resistance was moderately decreased due to acetylation (Fig. 8). On the other hand, refining also reduced the tear resistance. These results are attributed to reduced OH groups in acetylated specimens, reduction in H-bonds, and lower bonding among the fibers. It is known that acetylation increases stiffness of cellulose fibers (Drakhshande *et al.* 2007) and this may cause the decreasing trend of the tear index due to acetylation. Also, defragmentation due to acetylation and mechanical fracture in fibers due to refining may have possibly caused this reduction (Hubbe 2006).

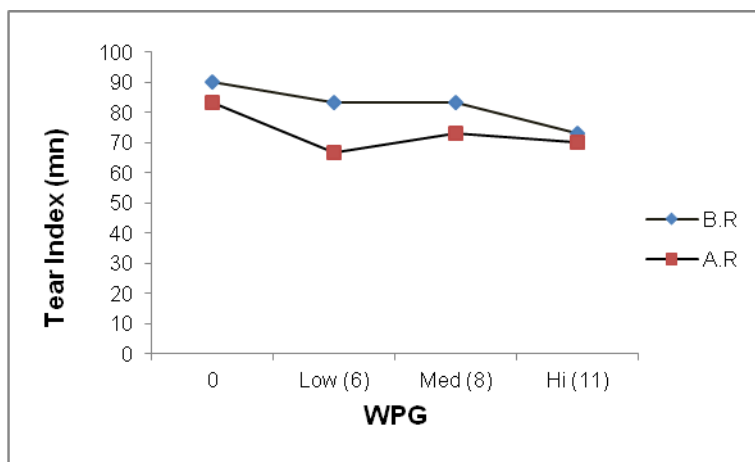


Fig. 8. Effect of reaction time of acetylation and refining on tear index of CMP paper

### Burst Strength

The burst strength of acetylated papers made from refined and non-refined pulp is presented in Fig. 9. It is evident that there were no obvious significant differences between non-treated, and low and medium intensity, but high-intense acetylated paper had significant differences in both refined and non-refined.

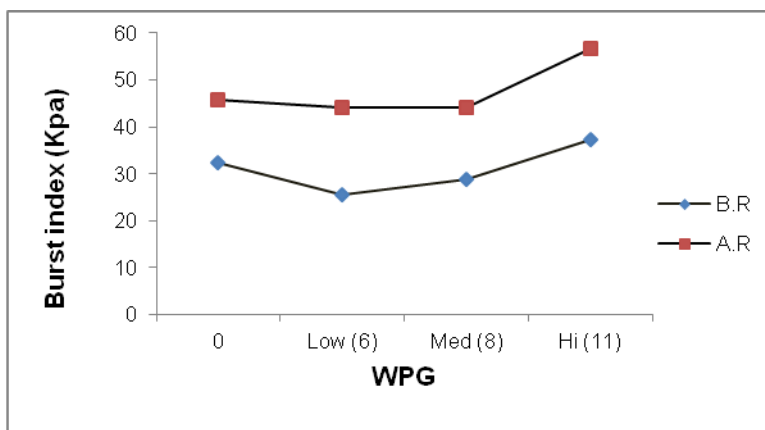


Fig. 9. Effect of reaction time of acetylation and refining on burst index of CMP paper

The highest values were obtained in the case of high-intense acetylation with increasing reaction time on refined paper. The results indicate that refining increased burst strength. This trend occurred with increasing reaction time. Refining caused an increase in flexibility of fibers.

## CONCLUSIONS

1. The results showed a significant improvement in physical and mechanical properties of the uncatylsed acetylated CMP paper, especially when the pulp was refined.
2. In accordance with other studies, we interpreted the effects of acetylation on the properties as a blockage of reaction sites. It was closely related to the decrease of the hydroxyl content as a result of substitution by acetyl groups.
3. Many studies have suggested that acetylation decreases some of the mechanical properties of paper, when the fibers (pulp) acetylated before paper-sheet making. However, we found that mechanical properties can be modified after the paper-making process, when the paper-sheet is acetylated instead of the fibers.
4. The reactions between functional groups can be divided into two parts. First, during the paper-sheet making process, the bonds between fibers can be easily created by partial of the bonding sites and these support the mechanical properties. Then, after paper-sheet making and during the acetylation process, the free bonding sites could be reacted and blocked by acetyl groups. The refining also increased the accessible bonding sites. Further, the strength per unit of bonded area of fibers was improved by the acetylation.

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