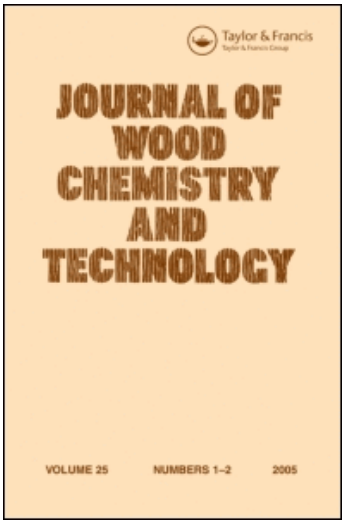

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ENHANCEMENT OF STRENGTH PROPERTIES OF MECHANICAL PULPS

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ABSTRACT

A new impregnation method to enhance strength properties of mechanical pulps in the absence of sulfonation treatment has been developed. Impregnation of groundwood, thermomechanical, and chemithermomechanical pulps with reactive ultrathin film-forming silane precursors has been investigated. Silane impregnation gave the treated pulps more than 20% increase in strength properties, but the pulp brightness dropped. The effect of impregnation time and temperature were studied. It was found that silane impregnation is highly effective under ambient temperature and pressure conditions, and the efficiency increased with increasing pulp temperature. In addition, the treated pulp demonstrated its advantages over an untreated one in terms of wet-end properties. The enhanced strength properties of silane-treated pulps are possibly due to an increase in fiber-to-fiber bonding.

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Key Words: Mechanical pulp; Impregnation; Silane; Strength; Wet-end properties

INTRODUCTION

Due to more stringent forest management and environmental regulations, ultra-high yield mechanical pulps have been increasingly used in paper industry. Except the advantages of high bulk, high opacity and good printing quality, purely mechanical pulps like thermomechanical pulp (TMP) have common weakness such as low strength and yellowing. On the other hand, good-strength bleached chemithermomechanical pulp (CTMP) with high-brightness has been replacing part of the bleached kraft pulp in some paper grades.[1] However, such an enhancement of strength performance from chemical treatment is usually obtained at the cost of printing properties and yield. Therefore, it would be desirable to develop a low-cost mechanical pulp with good strength without sulfonation treatment that could be used as a partial replacement for high-quality chemical pulps or CTMP in paper and board products.

Basic factors that influence the sheet strength properties of a pulp include[2]: individual fiber strength, interfiber bond strength, and the number of interfiber bonds (bonded area). For example, the CTMP process can yield a stronger pulp than the TMP process because the former can yield a higher portion of long undamaged fibers during fiberization, as weakening occurs at the primary cell wall layer and the middle lamella of the wood structure after chemical treatment. Besides, the sulfonic groups formed in the process are capable of participating in hydrogen bonding, which may increase fiber bonding in papermaking.[3]

Recent reports have indicated that self-assembling silane precursors can react with hydroxylated surfaces such as cellulosic fiber and hydroxylated inorganic compounds like glass fiber.[4] It is already known that hydroxyl groups present in cellulose can bond with Si-Cl, Si-S or Si-NH present in alkylsilanes due to catalysis by trace amounts of water that can adsorb on the hydrophilic cellulose surface.[5] Depending on the reactive functionality present in the alkylsilane derivatives, various surface properties can be imparted to the paper surface. Thus, treating mechanical pulp with reactive ultra-thin film-forming silane precursors can potentially provide a new way of improving the sheet strength. In this paper, we report on an investigation of treatment of mechanical and chemimechanical pulps with a series of silane precursors. The effects of these treatments on the properties of sheets prepared from the mechanical pulps were studied. The effects of the pretreatments on wet end characteristics, e.g., white water quality are also discussed.

EXPERIMENTAL

Groundwood of mixed softwoods (SGW), TMP of spruce, and CTMP of aspen were obtained from local mills. The pulps were screened and the latency was removed. The freenesses of the SGW, TMP and CTMP were 90, 128 and 300 CSF (Canadian Standard Freeness), respectively. The silane precursors chosen for this study were amino-substituted silane, namely, γ-aminopropyltriethoxysilane (AMS1100), γ-aminopropyltrimethoxysilane (AMS1110) and *N*-β-(aminoethyl)-γ-aminopropyltriethoxysilane (AMS1120). The chemical structures of the silanes are shown in Fig. 1. The silanes were dissolved in methanol and diluted to the desired concentration for the application.

Pulp Treatment

Our initial studies indicated that at low consistency with water as the medium, the effect of aminosilane impregnation on pulp sheet strength was almost zero. However the results improved significantly with methanol as the medium. On the other hand, trace water is important in silane treatment, functioning both as a reactive agent and a catalyst.[5] Thus, the pulp to be treated was first air-dried and washed with methanol to get rid of water contained in the pulp. The pulp moisture was adjusted to 4% by mixing with pure water, and then the consistency was adjusted to 0.1% with methanol. The pulp was treated separately with the three silanes, AMS1100, AMS1110, and AMS1120. Initial concentrations of the impregnation agent ranged between 0.01% and 12.5%, the treatment temperature was varied from 20 to 50°C, and the impregnation time varied from 3 min to 4 h. After impregnation, the pulp samples were washed thoroughly with methanol and dried before making handsheets. The amount of impregnation chemical consumed in each impregnation process was estimated by determining the

AMS1100: $H_2NCH_2CH_2CH_2Si(OCH_2CH_3)_3$

AMS1110: $H_2NCH_2CH_2CH_2Si(OCH_3)_3$

AMS1120: $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_2CH_3)_3$

Figure 1. Aminosilane structures.

total amine content of the impregnation solution before and after impregnation. It was found that the consumption of the impregnation chemical for a single pulp treatment cycle never exceeded 0.02%, as verified by using XPS and FTIR analyses.[6]

It was also confirmed, that recycling the methanol used in impregnation has no adverse effect.

X-Ray Photoelectron Spectrometry (XPS) Measurements

An XPS technique was used to characterize the surface chemical composition of unreacted and silane-reacted fiber. The method provides quantitative information about elemental composition. The XPS spectra were recorded using a Leybold Max 200 X-ray photoelectron spectrometer (Germany) with an unmonochromated Mg Kα source using excitation energy of 1253.6 eV. Atomic percentages of the elements present were derived from spectra run in a low-resolution mode. Binding energy and peak area were obtained after calibration to place the C1S peak at 285.0 eV. Detailed analytical techniques are discussed elsewhere.[6]

Other Analyses

Breaking length, burst index, and ISO brightness were measured according to Tappi test methods T404 om-87, T403 om-91, and T217 wd-77, respectively.[7–9] To test the effect of silane impregnation on wet-end properties of the treated pulp, fiber samples with talc as filler at 5 g/L consistency were analyzed for retention test in a dynamic drainage jar under moderate shear (1200 rpm). A commercial cationic polyacrylamide (0.1%) was added to promote retention. The talc retention values were determined according to T211 cm-86.[10] Charge demand of the white water from drainage was measured using colloidal titration technique and the suspended solids content was obtained following T656 cm-83.[11] FTIR spectra of untreated and AMS1000 treated TMP were also run.

RESULTS AND DISCUSSION

Papermaking Properties of the Treated Pulp

The efficiency of silanes in impregnation was compared by evaluating the breaking length of the control and impregnated pulps, as shown in

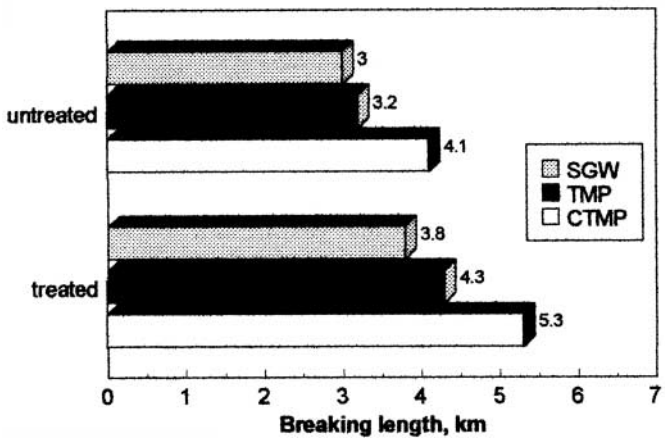

Figure 2. Effect of impregnation with AMS1100 on the breaking length of mechanical pulp sheets.

Fig. 2. The addition of AMS1100 improved breaking length of pulps independent of pulp types. Specifically, more than 25% strength improvement was achieved by the impregnation treatment. Also interesting to note, the Cobb sizing degree values indicate that there is a measurable decrease in the Cobb value of the treated sample relative to the control. However, one of the disadvantages for the treatment process is its limitation for use in bright paper products. The reaction of the aminosilanes with the pulps resulted in pulp yellowing, with a significant brightness drop as high as 4–6 points, depending on the initial pulp brightness.

Effect of Silane Concentration

Figure 3 shows that the initial concentration of aminosilanes in the impregnation treatment practically has no effect on the chemical up-take level by the pulp after it reaches 0.02% (on o.d. pulp), suggesting that the deposition of impregnation chemicals on the fiber surface is ultra-thin in nature.[6] However, it was observed that by increasing the concentration of the aminosilanes the retention time could be reduced significantly. The effect of the initial concentration of AMS1120 on the breaking length and burst index of TMP is also indicated in Fig. 3. Increasing the aminosilane concentration from 0.01 to 10% improved the breaking length by only 0.5 km. However, impregnation with only 0.01% AMS1120 caused the breaking length to increase from 3.2 km (Control) to 3.7 km. Similar to breaking

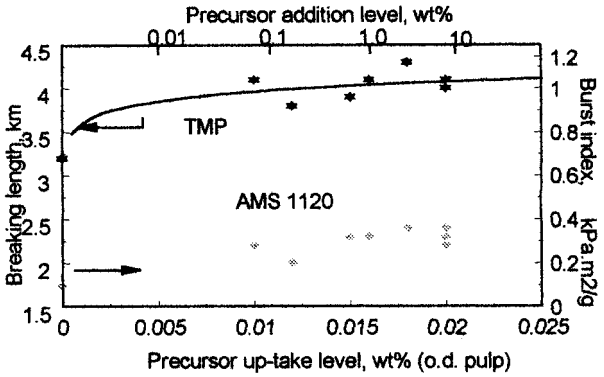

Figure 3. Effect of AMS1120 impregnation concentration on precursor consumption and strength properties of TMP.

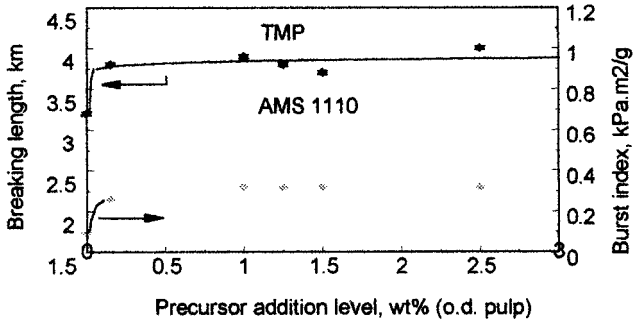

Figure 4. Impregnation concentration of AMS1110 vs. strength properties of TMP.

length, an increase in the burst index was also obtained by impregnating TMP with AMS1120. Again, an increase in the impregnation chemical concentration from 0.01 to 10% had a marginal influence on the burst index of the handsheet. A similar trend for the sheet mechanical properties was observed by impregnating TMP with AMS1110 (Fig. 4).

Effect of Impregnation Time

Figures 5 and 6 show breaking length as a function of impregnation time for SGW and TMP. In general, independent of the type of silane, the reaction is rapid. About 80% of the strength enhancement had been achieved within the first few minutes of impregnation. For impregnation

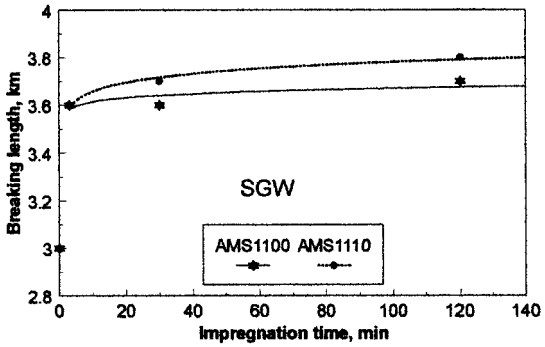

Figure 5. Impregnation time vs. the breaking length of SGW.

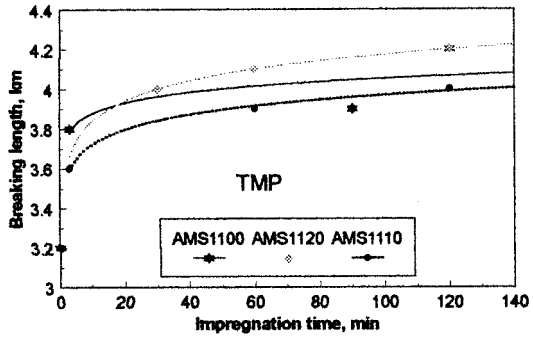

Figure 6. Impregnation time vs. breaking length of TMP.

of SGW pulp with AMS1110, a small amount of additional strength enhancement can be achieved by increasing the retention time (Fig. 5). Regarding TMP, Fig. 6 shows that AMS1120 is the most effective silane provided that a higher retention time is used. In contrast, the effect of AMS1100 on strength enhancement is practically independent of the retention time: a 30-min retention time was found to be optimum; however, a smaller retention time as low as 5 min could improve the breaking length by about 20%.

Effect of Impregnation Temperature

The effect of impregnation temperature on breaking length and burst index for AMS1110 impregnated TMP pulp is shown in Fig. 7. In general,

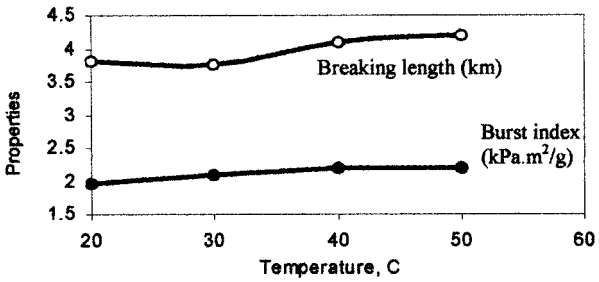

Figure 7. AMS1110 impregnation temperature vs. strength properties of TMP.

Table 1. Effect of Aminosilane Impregnation on Wet-End Properties of Mechanical Pulps

	TMP			SGW		
Properties	Control	AMS1110	AMS1120	Control	AMS1110	AMS1120
Talc retention, %	69	87	83	58	78	75
Strength retained, %	82	102	97	71	103	98
DDJ drainage rate, s/100 mL	10.3	11.2	11.0	11.2	12.3	12.5
Charge demand of white water, μeq/L	34	35	28	43	36	39
Suspended solid of white water, mg/L	1430	1159	1230	1569	1289	1338

temperature has a positive influence on chemical impregnation, and the same trend was observed for all aminosilane treated pulps. However, the increase in temperature and reaction rate does not follow a definite trend. With a high temperature, impregnation is effective for enhancing mechanical strength of fiber in a short retention time. It was found that an additional 10% increase in the burst and tensile properties could be obtained by increasing the temperature from 20 to 50°C.

Wet-End Properties of Impregnated Pulp

Table 1 shows the results of wet-end properties of mechanical pulps with impregnation treatment of aminosilanes, compared with that of untreated one. The treated pulp retained more talc (filler) than untreated

one. The high retention rate of fillers was also reflected in a low solid content of white water collected after drainage. However, the breaking length of treated pulp is 20% higher than a control one although the former has a higher content of ash. In addition, treated pulp improved wet end retention property over untreated pulp without significant increase in the drainage rate. It also reduced the cationic charge demand of white water. Therefore, it is not unlikely that chemical impregnation can further improve the paper making properties of a mechanical pulp.

Mechanism of Strength Improvement by Silane Impregnation

The increase in strength properties is possibly due to the strong interaction between the pulp and the impregnating silanes. Figure 8 shows FTIR spectra of untreated TMP and AMS-impregnated TMP after 30 min retention time. The detection of amine groups between 1510 and 1520 cm^{-1} indicates that aminosilane was still on the fiber surface even after the thorough methanol wash. Therefore, the amino-silane was probably chemically bonded to the fiber surface, but at very least strongly adsorbed. The results of the XPS measurement of treated pulp samples gave further evidence, as included in Table 2. Very low intensity but defined peak for nitrogen in XPS spectra demonstrates the deposition of aminosilanes on the fiber surface and low consumption of the impregnation chemicals. The silanes are probably deposited as a

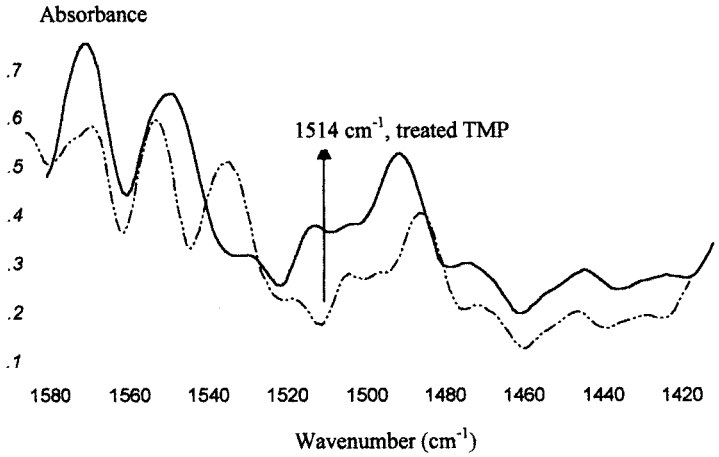

Figure 8. FTIR of untreated and AMS1110-treated TMP.

Table 2. XPS Peak Assignments of AMS1110

Elements	Assignment	AMS1110
N1s	−399.7	0.30
O1s	−532.5	32.58
C1s	−285.9	66.95

thin-film on the fiber surface. Our previous studies found that although surface roughness of pulp fibers prevents the formation of silane deposition with a uniform thickness, the impregnation thickness never exceeds 0.25 μm.[6]

The alkoxy groups in silanes are hydrolysable in the presence of water. The silanol groups formed from the hydrolysis can potentially undergo condensation, but definitely adsorption, resulting in the binding of silanols with hydroxyl groups on the fiber surface, as well as the formation of polysiloxane structures.[4] Consequently, fibers and fines are cross-linked through silanes to some extent and lead to an increased fiber-to-fiber bonding strength. Hence the strength properties of the silane-impregnated pulp are improved.

CONCLUSIONS

SGW, TMP and CTMP were modified by an impregnation treatment with silanes. The treatment improved breaking length by more than 20% at room temperature but decreased the pulp brightness. An increase in impregnation temperature had a positive effect on strength improvement. The handsheets prepared from the treated pulp showed more than 20% increase in the strength properties relative to untreated sheets made on a dynamic web-forming system, although the former had a higher filler content. It was found that the actual consumption of silanes is independent of initial concentration of silane after reaching a level of 0.02% (on o.d. pulp). The reaction for silane impregnation is fast, and about 80% of strength enhancement was obtained within the first few minutes.

The silanes deposited on the fiber surface can undergo hydrolysis and condensation reaction, leading to cross-linking between fibers and fines. The aminosilanes were probably chemically bonded to the fiber surface, as indicated by FTIR and XPS. Therefore, the enhancement of strength properties after silane treatment is a result of increased fiber-to-fiber bonding strength.

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