Chemical Modification of Lignin in High Yield Pulps-A New Approach to Improve Strength Properties And Bleachability

SINGH S.V.* SINGH S.P.* BHANDARI S.S.* AND SAINI B.K.*

ABSTRACT

The paper gives an account of the improvement achieved in strength properties and bleachability of high yield pulps through chemical modification of their lignin. Soda theremo mechanical (STM) and soda-sulphite thermomechanical (SSTM) pulps of bamboo and cold soda pulp of su-babul were modified using chlorine sodium sulphite and hypochlorite. Three combinations were employed: (i) chlorine/sulphite (ii) chlnrine/sulphite/hypochlorite and (iii) chlorine/sulphite/hypochlorite/sulphite/hypochlorite. It was observed that chlorine/sulphite/hypochlorite combination with 5.0% application of each chemical, gave optimum improvement in strength properties. in case of all the three types of high yield pulps used in this study at a brightness level of about 45. The improvement in strength properties recorded with STM pulp was as follows; tensile index rose from 22.07 to 30.48 N.m/g, burst index increased from 0.72 to 1.56 kPa, m^2/g. For SSTM pulp, the value of tensile index rose from 32.38 N.m/g to 42.96 N.m/g and burst index increased from 1,62 to 2.55 KPa. m^2/g. In case of cold soda high yield pulps of su-babul, similarly high degree of improvement was observed both in tensile index and burst index. The value of tensile index (11.37 N.m/g) and burst index (0.11 KPa, m^2 /g) rose to 28.34 N.m/g and 1.10 KPam^2/g, respectively. Washing of pulp between chlorination and sodium sulphite stages of treatment can be avoided without any impairment in strength properties of final pulp. However washing after sulphite and hypochlorite treatments is essential to achieve adequate level of brightness for newsprint furnish.

Development in pulp and paper production and the need for conservation of raw material call for studies on seeking technology for increasing the use of high yield pulps in papermaking furnishes. High yield pulps are rich in lignin which is hydrophobic in nature. On the one hand this makes the processing of high yield pulps more difficult and energy intensive and on the other there is deterioration in physical properties, such as bonding/surface strength, due to poor swellability of lignin-rich fibres. These drawbacks limit their use in papermaking. In order to enhance the use of high yield pulps, therefore, an attempt should be made to chemically modify their lignin with prime aim of increasing the hydrophilicity in the hope of improving the strength properties beatability and bleachability.

A few procedures for achieving such effects have been invstigated. These include oxidation with peracetic acid [1] and chlorine dioxide[1] or sulphonation with sodium sulphite[2,3]. Oxidation by peracetic acid or chlorine dioxide may not be economically feasible at present. Whereas the degree of sulphonation in high yield kraft pulp (60% yield with 20% lignin) achieved, even with 20% sulphite application, is very low[2].

In the experiments carried out on sulphonation of cold soda pulps of **Leucaena leucocephala** with sodium sulphite, it was found that the strength properties did not improve to any appreciable extent, even at 10% level of application of sodium sulphite. One reason for this is ascribed poor uptake of sulphite ion in lignin and thus making it not sufficiently hydrophilic. Bleaching of pulp to an adequate level of brightness required high percentage of hypochlorite as available chlorine. Due to this there was appreciable loss in pulp yield.

Therefore in an attempt to modify lignin in high yield pulps and to achieve a greater degree of hydrophilicity to improve their mechanical properties beatability and bleachability without impairment in pulp yield, a new approach was made to accomplish higher degree of sulphonation in lignin by chlorinating the pulp prior to sodium sulphite treatment followed by

*Forest Research Institute & Colleges, Dehradun

reaction with hypochlorite. Results of the experiments carried out on modification of lignin in high yield pulps prepared from bamboo *(Dendrocalamus strictus)* and su-babul *(Leucaena leucocephala)* are discussed in this paper.

EXPERIMENTAL

Preparation of high yield pulp :

Bamboo soda thermomechanical (STM) pulp and soda-sulphite thermomechanical (SSTM) pulp and su-babul cold soda (CS) pulp were used for studies on modification of lignin. For preparation of both STM and SSTM pulps bamboo chips were soaked with the liquor for 12 hr. keeping material to liquor ratio 1:3. For STM pulp 10% solution of caustic soda was used and for SSTM pulp the liquor used was 10% solution of caustic soda and sodium sulphite mixture, the ratio of NaOH to Na_2SO_3 being 4:1. The impregnated chips were processed in thermomechanical unit with preheater temperature of 120°C and retention time 3 min. The disc clearance being 0.3 mm. The yield of STM and SSTM pulps thus obtained was 80% and 85% respectively.

Cold soda pulp from su-babul was prepared by soaking chips in caustic soda liquor (50 gpl) for one hour keeping the material to liquor ratio 1:5 at 40°C. After one hour the chips were filtered off to remove excess liquor and soaked chips were refined in Sprout Waldern 12 inch disc refiner. The disc clearence in the three passes used for pulp preparation was 20,10 and 5 mil. The yield of cold-soda pulp of su-babul thus obtained was 80%.

Modification of lignin in high yield pulps :

All the three types of pulps (STM, SSTM and CS) were treated with chlorine, sodium sulphite and hypochlorite combinations. Three combinations were employed (i) chlorine/sulphite and (ii) chlorine/sulphite/hypochlorite (iii) chlorine/sulphite/hypochlorite/sulphite hypochlorite. In case of bamboo STM and SSTM pulps the conditions used for chlorination stage for combination (i) were: chlorine 2.5%, consistency 3.0%, time 10 min., Temp. 30°C. For treatment of chlorinated pulps with sodium sulphite and conditions were : sodium sulphite 5.0%, consistency 8.0%, tem. 80°C, time 1 hour. For combination (ii) the conditions for chlorination and sulphite treatment were same as used in combination (i) and the pulps obtained after reactions with chlorine and sodium sulphite were given hypochlorite treatment under the conditions : available chlorine 5.0% consistency 8.0%, temp. 45°C, time 2 hour and pH 10.5 $\pm$ 0.5.

In case of cold soda pulp from su-babul, modification with chlorine/sulphite combination was carried out at different levels of application of both chlorine and sodium sulphite (chlorine 2.5—5.0%, sulphite 5.0—10.0%). The other conditions during chlorination and sulphite treatment were kept same as used for modification of bamboo pulps, excepting that consistency during sulphite treatment was maintained at 5.0%. For chlorine/sulphite/hypochlorite combination, the doses of chemicals used were : chlorine 2.5—5.0%, sulphite 5.0—10.0% and hypochlorite 5.0—10.0%. The other conditions during chlorination and sulphite treatment were the same as employed with earlier combination. During hypochlorite treatment the other conditions were : consistency 5.0%, time 1 hr., temp. 45°C, pH 10.5 $\pm$ 0.5. In case of chlorine/sulphite/hypochlorite/sulphite/hypochlorite combination, chemical doses for chlorine, sulphite (1) and hypochlorite (1) stages were : chlorine 2.5—5.0%, sulphite 5.0% and hypoehlorite 5.0%. The percentage of chemicals used in sulphite (2) and hypochlorite (2) stages were : sulphite 3.0—8.0% and hypochlorite 2.0%. The other conditions were same as used for chlorine/sulphite/hypochlorite combination.

Pulp Evaluation :

The pulps were evaluated for strength properties (tensile index, burst index and tear index) using standard procedures employed for sheet making/air drying and testing of handsheets. For sheetmaking/air drying standard British sheet making system was used and testing was done as per ISO standards as usual.

RESULTS AND DISCUSSION :

The data on strength properties of soda thermomechanical and soda-sulphite thermomechanical high yield pulps prepared from bamboo (STM and SSTM) and those of modified pulps obtained via chlorination/sulphite/hypochlorite combinations are recorded in Table—1, Whereas the strength properties data on untreated and modified cold soda pulps prepared from su-babul are given in table—2.

TABLE — 1

Strength properties of handsheets of Bamboo STM SSTM and modified pulps*

Pulp type and modification	Tensile index N.m/g	Burst index KPa.m²/g	Tear index m N.m²g
STM-untreated	22.07	0.72	5.37
STM-Chlorine/sulphite	27.94	1.20	5.43
STM-Chlorine/sulphite hypochlorite	30.48	1.56	7.07
SSTM-Untreated	32 38	1.62	7.85
SSTM-Chlorine/sulphite	38.84	2.11	9.02
SSTM-Chlorine/sulphite/ hypochlorite	42 96	2.55	8.98

*pulps were beaten in P.F.I. Mill at 800 Rev (C.S.F. about 300 ml)

TABLE — 2

Strength Properties of Hand Sheets of Modified Cold Soda Pulp of Su-babul*

Treatment	Tensile Index N. m/g	Burst Index KPa.m²/g	Tear Index m N.m²/g	SO_3^{--} Consumed %	Brightnes %	Opacity %
Blank	11.37	0.11	2.35	—	38.0	99.5
5% Sulphite	13.56	0.19	2.57	4.88	43.2	99.2
CHLORINATION/SULPONATION						
2.5% Cl_2, 5% SO_3^{--}	14.00	0.40	2.74	4.83	—	—
2.5% Cl_2, 8% SO_3^{--}	21.97	0.74	2.80	7.75	42.6	99.8
2.5% Cl_2, 10% SO_3^{--}	19.59	0.62	2.84	9.61	42.8	99.5
5% Cl_2, 5% SO_3^{--}	20.74	0.75	2.93	4.92	38.8	99.3
5% Cl_2, 8% SO_3^{--}	19.71	0.65	2.95	7.84	40.4	97.9
5% Cl_2, 10% SO_3^{--}	20.83	0.58	3.14	9.66	41.5	98.9
CHLORINATION/SULPONATION/HYPOCHLORITE						
2.5% Cl_2, 5% SO_3, 5% Hypo	15 60	0.44	2 90	4.87	—	—
5% Cl_2, 5% SO_3, 5% Hypo	28.34	1 10	3.11	4 92	44.2	99.5
5% Cl_2, 8% SO_3, 5% Hypo	21 65	0 92	3.41	7.72	47.2	98.6
5% Cl_2, 8% SO_3, 8% Hypo	19 95	0 79	3.15	7.75	49 2	98.8
5% Cl_2, 10% SO_3, 5% Hypo	19.87	0.64	2 96	9.65	47.2	98.6
5% Cl_2, 10% SO_3, 10% Hypo	24 74	0 88	3 41	9.66	51.6	98 9
CHLORINATION/SULPHONATION$_1$/HYPOCHLORITE$_1$/SULPHONATION$_2$/HYPOCHLORITE$_2$						
2 5% Cl_2, 5% SO_3, 5%H, 3%SO_3, 2% Hypo	19.63	0.64	2.71	7.9	47.2	99.1
2 5% Cl_2, 5% SO_3, 5%H, 5%SO_3, 2% Hypo	19.32	0.60	2.87	9.8	49.2	98 8
2.5% Cl_2, 5% SO_3, 5%H, 8%SO_3, 2% Hypo	17.92	0 47	2 71	12.7	48.2	99.0
5% Cl_2, 5% SO_3, 5%H, 3%SO_3, 2% Hypo	22.11	0.82	2 98	7.9	48.6	99.0
5% Cl_2, 5% SO_3, 5%H, 5%SO_3, 2% Hypo	222.2	0.74	2.96	9.8	47.7	99.1
5% Cl_2, 5% SO_3, 5%H, 8%SO_3, 2% Hypo	23.19	0.72	3.02	12.7	49.0	99.0

*Pulps were beaten in Lampen mill at about 150 ml CSF.

Bamboo STM/SSTM Pulps

In case of bamboo, treatment of STM pulp with chlorine/sulphite combination increased the tensile index from 22.07 to 27.94 N.m/g and the burst index from 0.72 to 1.20 KPa.m²/g. Use of chlorine/ sulphite/ hypochlorite combination resulted in much greater improvements the tensile index rose to 30.48 N.m/g and the burst index to 1.56 KPam²/g. Similarly for SSTM pulp, these treatments gave highly improved pulps. While treatment with chlorine/sulphite combination increased the tensile index from 32.38 to 38.84 N m/g and the burst index from 1.62 to 2.11 KPa.m²/g, treatment with chlorine/sulphite/hypochlorite combination rose the value of tensile index to 42 96 N.m/g and burst index to 2.55 KPa.m²/g. The tear index of SSTM pulp rose to 9.00 from 7.85 mN.m²/g irrespective of the combination of chemicals employed for modification or treatment. In case of STM pulp there was no change in the value of tear index (5.37 mN.m²/g) with chlorine/sulphite combination, whereas with chlorine/sulphite/hypochlorite treatment the value rose to 7.07 m N.m²/g.

Su-babul cold soda pulp :

In modification of cold soda pulp of su-babul, the effect of variation of percentage of chlorine, sulphite and hypochlorite was studied in each type of combination, so as to find out optimum doses of chemicals required to achieve highest degree of improvement in strength properties at adequate level of brightness for use in newsprint furnish.

A perusal of data on strength prope ties of modified cold soda pulp of su-babul indicates that for chlorine/ sulphite combination the optimum doses of chemicals are : chlorine 5.0% and sodium sulphite 5.0% under these optimum conditions the tensile index increased from 11.37 to 20.74 N.m/g, the burst index rose from 0.11 to 0 75 KPa.m²/g and the tear index increased from 2.35 to 2.93 m N.m²/g. The data on strength properties of pulp modified with the sequence chlorine/ sulphite/hypochlorite shows that the optimum percentage of chemicals were; chlorine 5.0%, sodium sulphite 5.0% and hypochlorite 5.0%. The values of tensile index, burst index and tear index rose to 28.34 N. m/g, 1.10 KPa.m²/g and 3.11 m N.m²/g, respectively. In the modified pulps obtained using chlorine/sulphite/ hypochlorite/sulphite/hypochlorite, it is noticed that application of second stage of sulphite and hypochlorite resulted in reduction in all the strength properties. This indicate that application of second stage of both sulphite and hypochlorite is unwarranted. Modification with the best combination that is, chlorine/sulphite/hypochlorite improved for the brightness of pulp from 38 to 44.2, which may be adequate for use in newsprint furnish.

Effect of Eleminating Inter-stage Washing

During all the three types of combination used for modification of high yield pulps, the pulps after each stage of treatment is washed with water before giving next treatment. Since this involves use of washers at each stage and huge amount of water as well, it was considered appropriate to examine the effect of eliminating interstage washing altogether. It was observed that there was no adverse effect on strength properties of pulp modified by chlorine/sulphite/hypochlorite combination, when unwashed chlorinated pulp is passed on for sulphite treatment. But after sulphite treatment washing is essential for brightness development. Interstage washing between chlorination and sulphite treatment could be avoided.

Reaction of Lignin During Modification :

It was observed that uptake of sulphite by unchlorinated pulps was very low. The chlorination of all types of high yield pulps increased the uptake of sulphite. Due to higher uptake of sulphite by pulp, the hydrophilicity of lignin increases which results in improved pulps in respect of their tensile index and burst index. Increase in tear index is another remarkable feature of the modification with chlorine/sulphite/ hypochlorite combinations. Treatment of pulps already modified by chlorine/sulphite combination with hypochlorite further improves the tensile index and burst index. This may be ascribed to part oxidation of modified lignin resulting in its degradation.

By chlorination of high yield pulps the lignin in them undergoes nuclear as well as side chain substitution of chlorine and oxidation. The oxidation of lignin results in quinone structure formation. Quinones are known to rapidly react with sulphite through adduct formation. In this way chlorination of high yield pulps prior to sulphite treatment increases the uptake of

sulphite and thereby improving the hydrophilicity of lignin and consequently the strength properties. As the reactions with chlorine and sodium sulphite are of additive nature there was little impairment in the yield of modified pulps.

CONCLUSION :

It could be thus concluded that chlorination prior to sulphite treatment followed by reaction with hypochlorite improves the bonding/strength properties of high yield pulps to a great extent. In case of bamboo STM pulp the increase in tensile index was 38%. Burst index increased by over 100%. For SSTM pulp the tensile index increased by 33% and burst index by 57%. In case of su-babul cold soda pulp the increase in tensile index was 150%. The final brightness developed by hypochlorite treatment was about 44 in case of both Bamboo and subabul pulps. Further work on modification of high yield pulps from other hardwoods, commercial samples of high yield pulps and on kinetics of each stage of the best combination that is chlorine/sulphite/hypochlorite are in progress and would be reported in due course.

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