ENHANCEMENT OF OPTICAL PROPERTIES OF BAGASSE PULP BY *IN-SITU* FILLER PRECIPITATION

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In-situ precipitation of calcium carbonate in bagasse fibers resulted in a very significant increase in specific scattering coefficient and consequently large improvements in opacity and brightness of the handsheets made from such pulp. At the same level of filler loading, the scattering coefficient of *in-situ* precipitated pulp was much greater than for directly loaded pulp. *In-situ* precipitation of calcium carbonate caused a drop in strength properties of bagasse pulp, but such loss could be recovered to a large extent by blending with other pulps. The effect of *in-situ* precipitation of calcium carbonate on pulp fibers was quite different for bagasse pulp from hardwood pulp. *In-situ* precipitation of calcium carbonate on hardwood fibers showed neither much improvement in optical properties nor much reduction in strength properties.

Keywords: Fiber loading; In-situ precipitation; Bagasse pulp; Filler; Scattering coefficient; Pulp blending

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INTRODUCTION

Bagasse is an important fibrous raw material for papermaking in India and other Asian nations where the supply of forest-based raw material is not adequate. Bagasse pulps are capable of producing papers with excellent formation, surface smoothness, and sufficient strength as required in many grades of paper. However, relatively low optical scattering power has been considered a major drawback of bagasse fibers. It has been generally observed that the papers that have a higher percentage of chemical bagasse pulp in their furnish have relatively lower opacity, lower bulk, and higher print-through tendency. A low print-thorough is an extremely important requirement for papers that are used for printing on both sides.

Opacity can generally be increased by using more filler in paper, although with usually some reduction in paper strength and stiffness. However, for bagasse pulps, the observed improvements in optical properties are not as significant as the reduction in strength properties. New developments, such as incorporation of filler particles within the fiber lumen and/or cell wall, can offer new opportunities to improve paper properties. The filler can be incorporated in a paper sheet by three different techniques:

1. Direct loading of filler with fibers, which is the most frequently used technique by paper mills
2. Loading of filler within the fiber lumen by mechanical diffusion of filler particles through the bordered pits
3. *In-situ* precipitation of filler in fiber lumen and/or cell wall

Methods for incorporating fillers inside the fiber lumen have been studied extensively. Green *et al*. (1982) and Middleton and Scallan (1985) studied loading of fiber lumens with titanium dioxide particles by mechanical diffusion, in which the slurry consisting of softwood fibers and titanium dioxide was stirred over a period of time. Many other investigators followed similar approach using precipitated calcium carbonate (PCC) in place of titanium dioxide (Middleton *et al*. 2003; Miller and Paliwal 1985; Petlicki and van de Ven 1994). The lumen loading resulted in paper sheets having better formation and strength properties than the conventionally loaded sheets at equal filler levels. Allan *et al*. (1992a) point out that although the approach of lumen loading was theoretically promising, the technique was limited to pigments having small enough particle size to pass through the pit apertures of the fibers to reach the lumen. They suggested that the filler particle could be incorporated within the cell wall voids (as high as 1.5 mL/g of pulp) by *in-situ* precipitation of insoluble inorganic materials.

Allan *et al*. (1992b) and Silenius (1996) have reviewed several studies on cell wall loading by *in-situ* precipitation of a filler pigment. Usually the approach has been to use two soluble salts. The pulp fibers are saturated with one salt, and the other soluble salt is added to these saturated fibers to effect the precipitation of an insoluble inorganic material. For example, Allan *et al.* (1992a) used nickel chloride and sodium carbonate solutions to precipitate nickel carbonate. Craig (1952) used calcium chloride to saturate the fibers, while sodium carbonate solution was added to precipitate calcium carbonate *in-situ*. Thomson (1962) modified the Craig's approach and added ammonium carbonate solution to the fibers saturated with calcium chloride. The soluble by-product, sodium chloride or ammonium chloride, was flushed out with water. When loaded fibers were used in papermaking, Klungness *et al.* (1993) observed that the opacity of the paper was improved, but the strength was reduced. A Japanese patent (Yoshida *et al*. 1987) describes a method of fiber wall loading that yields no by-products other than water. In this method, calcium carbonate is precipitated by bubbling carbon dioxide gas through slurry of calcium hydroxide and pulp. Klungness *et al*. (1996, 1999, 2000) used the same approach in their experiments. Subramanian *et al*. (2007) followed a slightly different approach in which they first prepared composite fillers by treating a mixture of pulp fines and calcium hydroxide suspension with carbon dioxide gas to precipitate calcium carbonate. This PCC-cellulose composite was then used as filler for loading the paper. They observed that, for given filler content in paper sheet, the bending stiffness, internal bond strength, and tensile index were greater for sheets loaded with PCC-cellulose composite than the sheets conventionally loaded with PCC. However, the light scattering coefficient of the PCC-cellulose composite filler loaded sheets was somewhat lower than that of conventionally loaded sheets. Chauhan *et al*. (2007) loaded hardwood pulp fibers by *in-situ* precipitation of sodium aluminosilicate.

Although substantial disagreement exists, the general view is that the paper made of pulp in which the filler has been incorporated within fibers exhibits greater tensile, burst, and tear strength than corresponding conventionally filled paper (Allan 1995; Miller and Paliwal 1985; Fujiwara 1993). Several other advantages of *in-situ* precipitation (Allan 1995) include easier white water management due to improved retention, reduction in the dosages of expensive polymeric retention aids, easier drying of paper due to reduced collapse of fiber voids, decreased abrasion damage to the forming fabric, less dusty paper, and smaller two-sidedness in paper because the filler is inside the fiber. However, at equal levels of filler loading, significant improvements in optical properties of paper have not been reported. The optical properties of paper made of lumen- or cell wall-loaded pulp are in general equal to those of conventionally loaded paper (Allan *et al*. 1992b; Green *et al*. 1982; Chauhan *et al*. 2007).

Allan *et al*. (1998) have shown that the *in-situ* precipitation of filer within the fiber wall could be utilized to obtain gains in optical properties of a newsprint furnish consisting of blends of semichemical soda bagasse pulp and semibleached kraft softwood pulp at equal strength levels. However, at equal filler levels, the scattering coefficient values were slightly less for the fiber-wall loaded sheets than for the conventionally loaded sheets.

In the present work we have studied the effect of *in-situ* precipitation of $CaCO_3$ in bleached bagasse chemical pulp fiber. The result obtained were somewhat different from the finding of the earlier studies reported in the literature. It was observed that at equal ash levels, the bagasse pulp with calcium carbonate precipitated on fibers *in-situ* showed a significantly greater improvement in light scattering coefficient than precipitated calcium carbonate filler directly added to the pulp. However, the *in-situ* precipitation of calcium carbonate on fibers caused a significant loss of pulp strength. Ways to enhance the strength of these weakened pulps by methods such as use of strength aids, blending with stronger fibers, and refining after *in-situ* precipitation have also been studied.

EXPERIMENTAL WORK

Never-dried bleached bagasse, hardwood, and wheat straw pulps were obtained from three different integrated pulp and paper mills in India. The bleached softwood pulp was a commercial pulp in the form of dried sheets. The pulps were beaten in a PFI mill (TAPPI suggested practice T-248) to 32 °SR value. The bagasse and hardwood pulp fibers were loaded by *in-situ* precipitation of calcium carbonate. The beaten pulp was soaked in sodium carbonate solution in a 3-L beaker fitted with a laboratory agitator operating at 1200 to 1500 rpm. After about 20 minutes time for penetration of Na_2CO_3 into the fibers, a saturated $Ca(OH)_2$ solution (1.46 g/L) was added to the mixture for precipitation of $CaCO_3$. The stirring in the beaker was continued for another 20 min. After the precipitation, the pulp was washed thoroughly with running tap water over a 250-mesh screen until a clear filtrate was obtained.

Standard handsheets were prepared from the *in-situ* precipitated bagasse and hardwood pulps and blends of bagasse pulp with wheat straw and softwood pulps in different proportions. The handsheets of 60 g/m^2 were prepared in a laboratory sheet former with a square cross section, 165mm x 165mm, according to the standard method SCAN C: 26. The handsheets were air dried in contact with glaze plates. The handsheets were internally sized by AKD to give $Cobb_{60}$ sizing test values of about 22 g/m^2.

For comparison, standard handsheets were also prepared from bagasse and hardwood pulps with direct addition of a commercial filler grade precipitated calcium carbonate (PCC) pigment and a retention aid obtained from a local chemicals supplier.

The brightness, opacity, specific scattering coefficient, and specific absorption coefficient of handsheets were determined from the measurements on Elerpho spectrophotometer (L&W Model 071). The ash content, grammage, thickness, tensile strength, burst strength, tear strength, folding endurance and $Cobb_{60}$ values for the handsheets were determined using appropriate SCAN methods. A few scanning electron micrographs were taken for observing the location of the precipitated calcium carbonate in the sheets. The physical properties of the pulps used in the study are given in Table 1.

Table 1. Physical Properties of the Pulps Used

Property*	Bagasse	Hardwood	Softwood	Wheat straw
Ash, %	0.61	0.66	0.35	1.60
Tensile index, Nm/g	58.9	65.6	44.1	45.5
Burst index, kPa m^2/g	3.73	4.73	5.96	2.66
Tear index, mNm^2/g	3.96	5.34	18.5	3.32
Folding endurance	1.39	1.47	2.69	0.62
Brightness, %	73.5	73.0	74.3	71.4
Scattering coefficient, m^2/kg	21.2	36.7	24.0	25.8
Absorption coefficient, m^2/kg	0.52	0.73	0.38	0.62
*The properties were evaluated from standard handsheets made after beating the pulps to 32 °SR in a PFI mill.				

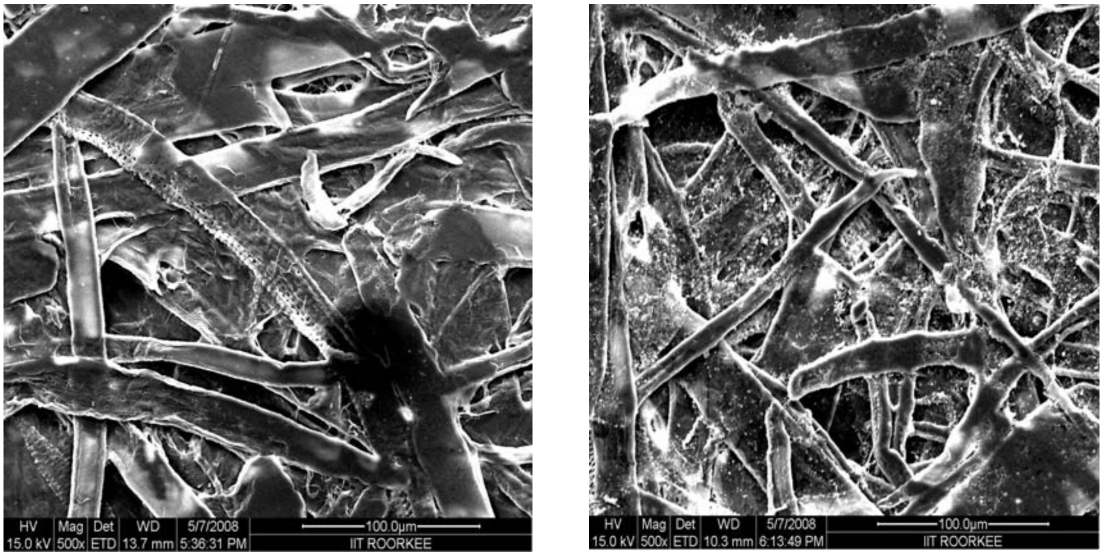
RESULTS AND DISCUSSION

Scanning Electron Micrographs of Handsheets

Figure 1 shows scanning electron micrographs (SEM) of bagasse handsheets without filler loading, with direct filler loading, and with fiber loading by *in-situ* precipitation. These micrographs confirm that a large proportion of the $CaCO_3$ was precipitated inside the fiber lumen or/and cell wall during the *in-situ* precipitation process. For direct loading (Fig. 1b), the filler particles were present on the fiber surfaces, while for *in-situ* precipitation (Fig. 1c), most of the precipitated filler particles were present inside the fibers, as most of the particles precipitated outside the fibers were removed by washing. Figure 1d shows the cross section of a bagasse fiber with a large number of precipitated $CaCO_3$ particles inside it.

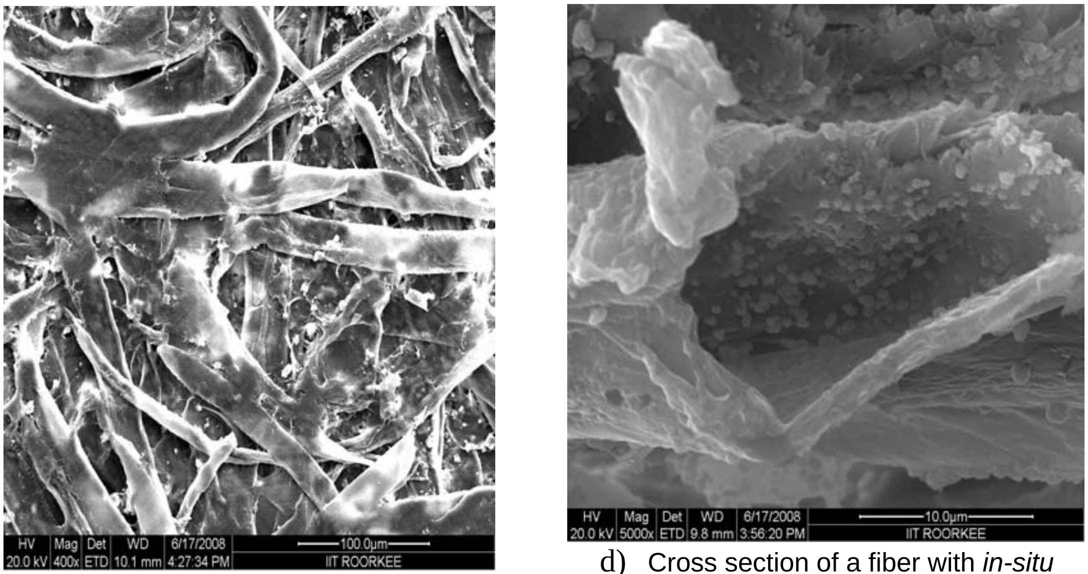
Effect of Filler on Optical Properties of Handsheets

Figure 2 shows the effect of increasing amount of precipitated $CaCO_3$ filler on the specific scattering coefficient, brightness, and opacity of the bagasse and hardwood handsheets. At zero filler level, the scattering coefficient of bagasse handsheets was much lower than that of hardwood handsheets. Direct filler loading resulted in a marginal increase in the scattering coefficient for both bagasse and hardwood handsheets, while the fiber loading by *in-situ* precipitation resulted in a much greater increase, particularly for the bagasse handsheets. Both the bagasse and the hardwood pulps had nearly the same values of the scattering coefficient for ash content greater than about 12%.



a) Without filler loading

b) Direct addition of PCC filler



c) *In-situ* precipitation of $CaCO_3$

d) Cross section of a fiber with *in-situ* precipitated $CaCO_3$

Fig. 1. SEM micrograph of handsheets of bagasse

The brightness and opacity of the handsheets made of bagasse fibers loaded by *in-situ* precipitation showed a very significant improvement because of the large increase in its scattering coefficient. To eliminate the effect of variation in the grammage of the handsheets, the values of opacity used in Fig. 2 were calculated for a grammage of 60 g/m^2 using the values of *s* and *k*, and the simplified Kubelka-Munk equations (Bierman 1996).

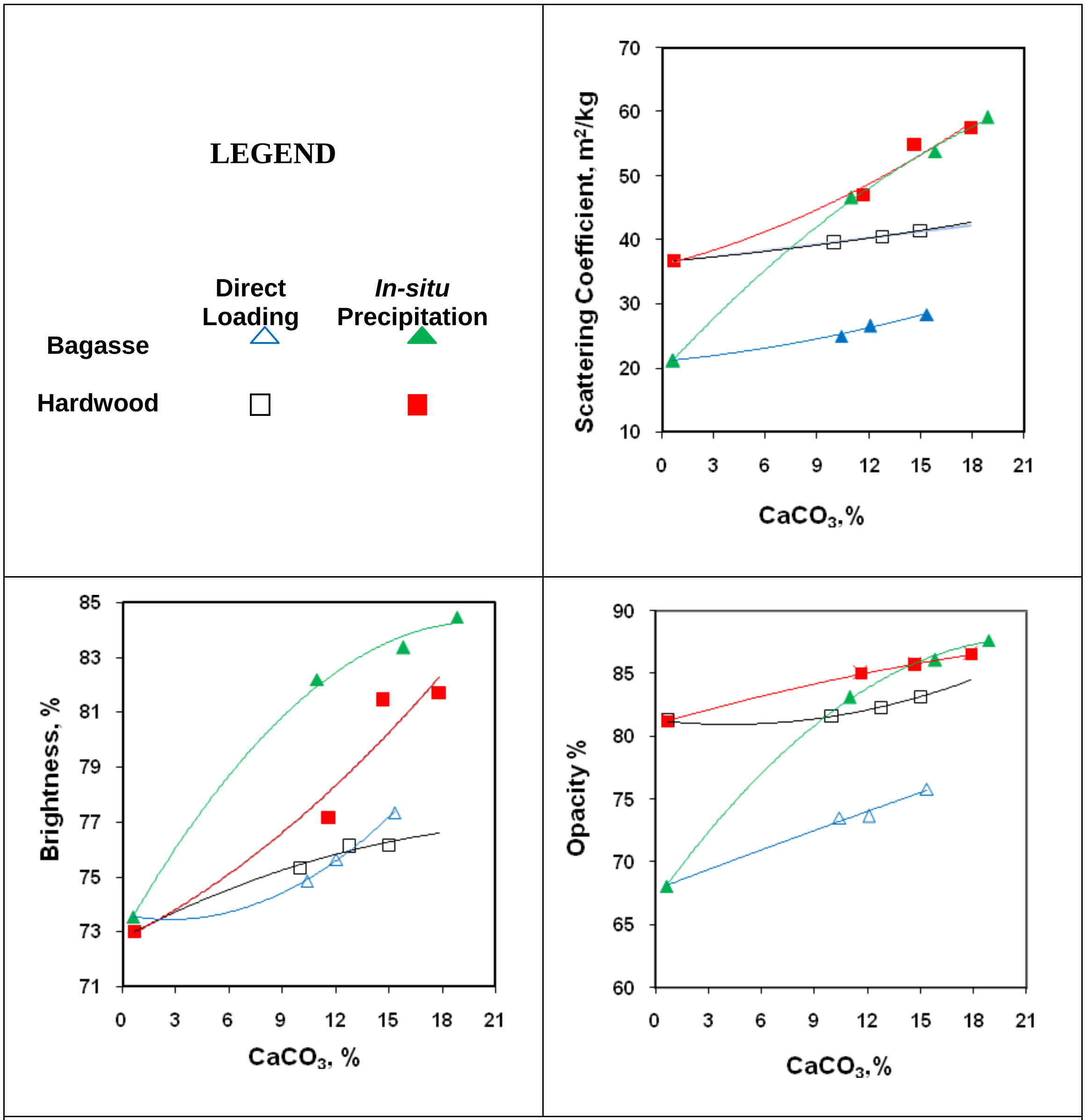


Fig. 2. Effect of filler on optical properties of the handsheets at different $CaCO_3$ levels. Opacity values were calculated for a constant grammage of 60g/m^2 using simplified Kubelka-Munk equation.

Effect of Filler on Strength Properties

In-situ precipitation of calcium carbonate on pulp fibers caused a greater reduction in most of the strength properties for both bagasse and hardwood pulps than the reduction caused by the direct addition of precipitated calcium carbonate. Figure 3 shows the effect of filler loading on the tensile index, folding endurance, and tear index of paper. The tensile index decreased with increasing amount of filler for both direct loading and loading by *in-situ* precipitation. The decrease in tensile index was much greater in the case of *in-situ* precipitation than in case of direct filler loading. The folding endurance showed a trend similar to that of the tensile index. The effect of filler level on the tear strength of handsheets was small for both direct loading and *in-situ* precipitation.

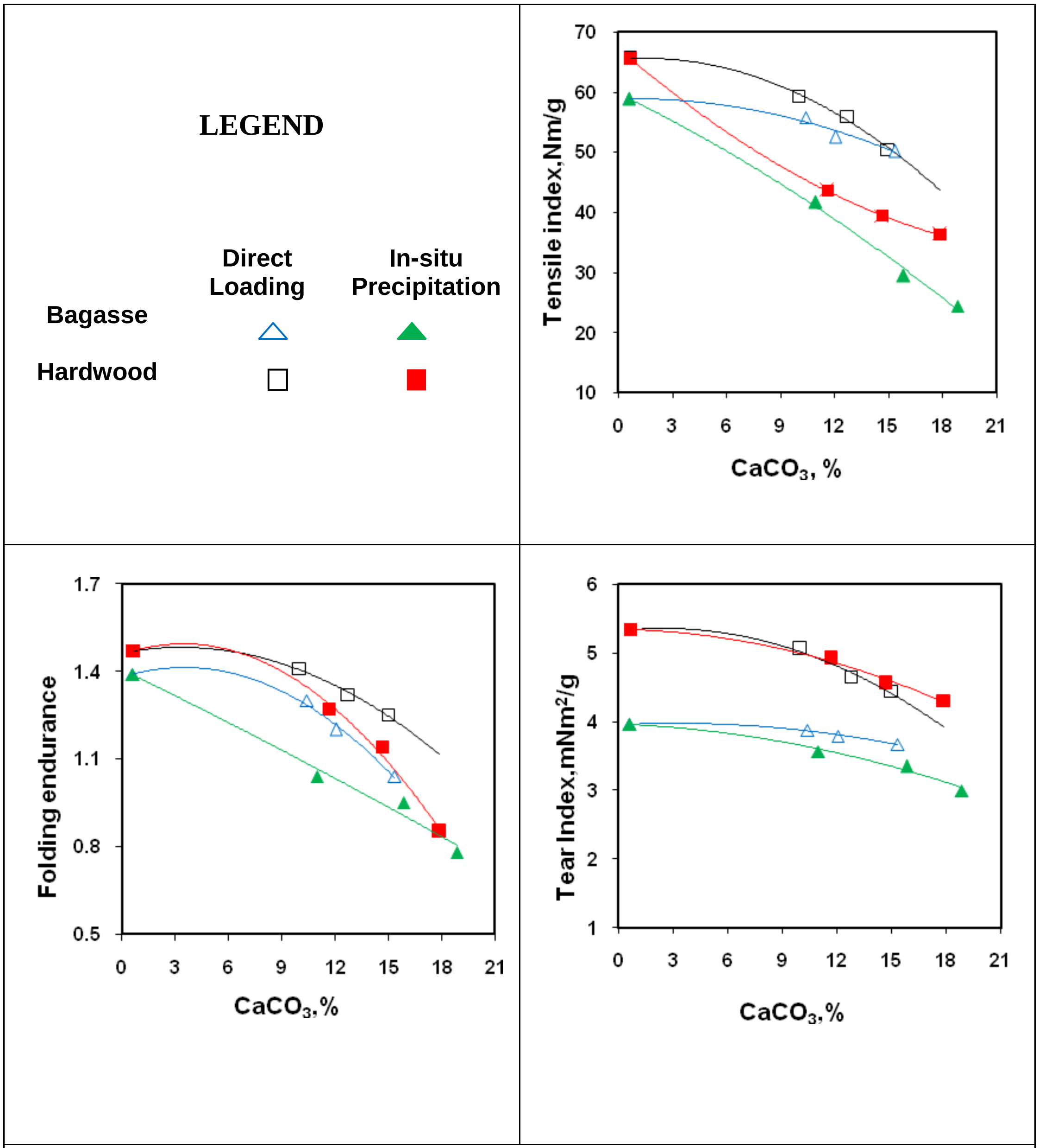


Fig. 3. Effect of filler on Strength properties of the handsheets at different $CaCO_3$ levels

Enhancement of Strength of *In-situ* Precipitated Bagasse Pulp Fibers

In-situ precipitation of calcium carbonate in bagasse paper handsheets gave the desired improvement in optical properties, but caused undesired reduction in strength properties of the sheets. Several options aimed at overcoming the drawback of low strength of *in-situ* precipitated bagasse pulp were evaluated. In the experiments for *in-situ* precipitation of $CaCO_3$, the solution of $Ca(OH)_2$ was added to pulp that had been soaked in a solution of Na_2CO_3, with the belief that this procedure will allow a greater precipitation of $CaCO_3$ in the fiber lumen than on the external surfaces of the fiber, in spite of very low solubility of $Ca(OH)_2$ in water. Later, a few experiments were conducted in reverse order of the chemicals addition. The pulp fibers were soaked in $Ca(OH)_2$ solution, and $CaCO_3$ was precipitating by bubbling CO_2 gas through the pulp. It was found that the order of chemicals addition was not important in this case, as the results were not different, both for scattering coefficient as well as for strength.

Blending of other pulps with in-situ precipitated bagasse pulp

Experimental trials were conducted to evaluate the reinforcing effect of different grades of pulp when blended with the weakened *in-situ* precipitated bagasse fibers. Softwood, hardwood, and wheat straw pulps were blended with the *in-situ* precipitated bagasse pulp having 18.86% $CaCO_3$ loading. Figure 4 shows the effect of blending of other types of pulp on paper properties. At smaller proportions of blending (< 20%), wheat straw pulp gave the best enhancement in the tensile strength, presumably due to its high hemicelluloses content, while the long-fibered softwood pulp was the best in enhancing the tear strength, folding endurance, and burst strength. The addition of blending pulps will decrease the filler content in the blends. For example, at 20% addition of blending pulps, the filler content will be reduced from 18.86% to about 15%. It may be noted that the improvement in tensile strength due to blending was much greater than the strength of the fiber loaded bagasse pulp at the same level of filler content. The reductions in the scattering power due to blending of pulps were of the same order as the reduction due to reduced filler content in the filler-loaded bagasse pulp. Thus, it can be said that the blending of either of the pulps yields significant recovery in strength without losing greatly in the optical properties.

Refining of in-situ precipitated bagasse pulp

It was observed that the freeness of bagasse pulp increased during *in-situ* precipitation of $CaCO_3$. The °SR of the pulp decreased from about 32 to about 15. The *in-situ* precipitated pulp was refined once again to 32 °SR to check if this could recover some of the strength lost during *in-situ* precipitation. As shown in Figure 5, on refining the *in-situ* precipitated bagasse pulp, the tensile index values approached the same levels as those of direct loaded pulp while showing only a small reduction in the scattering coefficient. There was not much effect of this refining on tear strength of the pulp. The increase in pulp freeness during *in-situ* precipitation could be due to stiffening of the fibers as the filler precipitated inside the cell wall. On refining, the flexibility of the fibers could be restored, resulting in recovery of the tensile strength without much decrease in scattering coefficient.

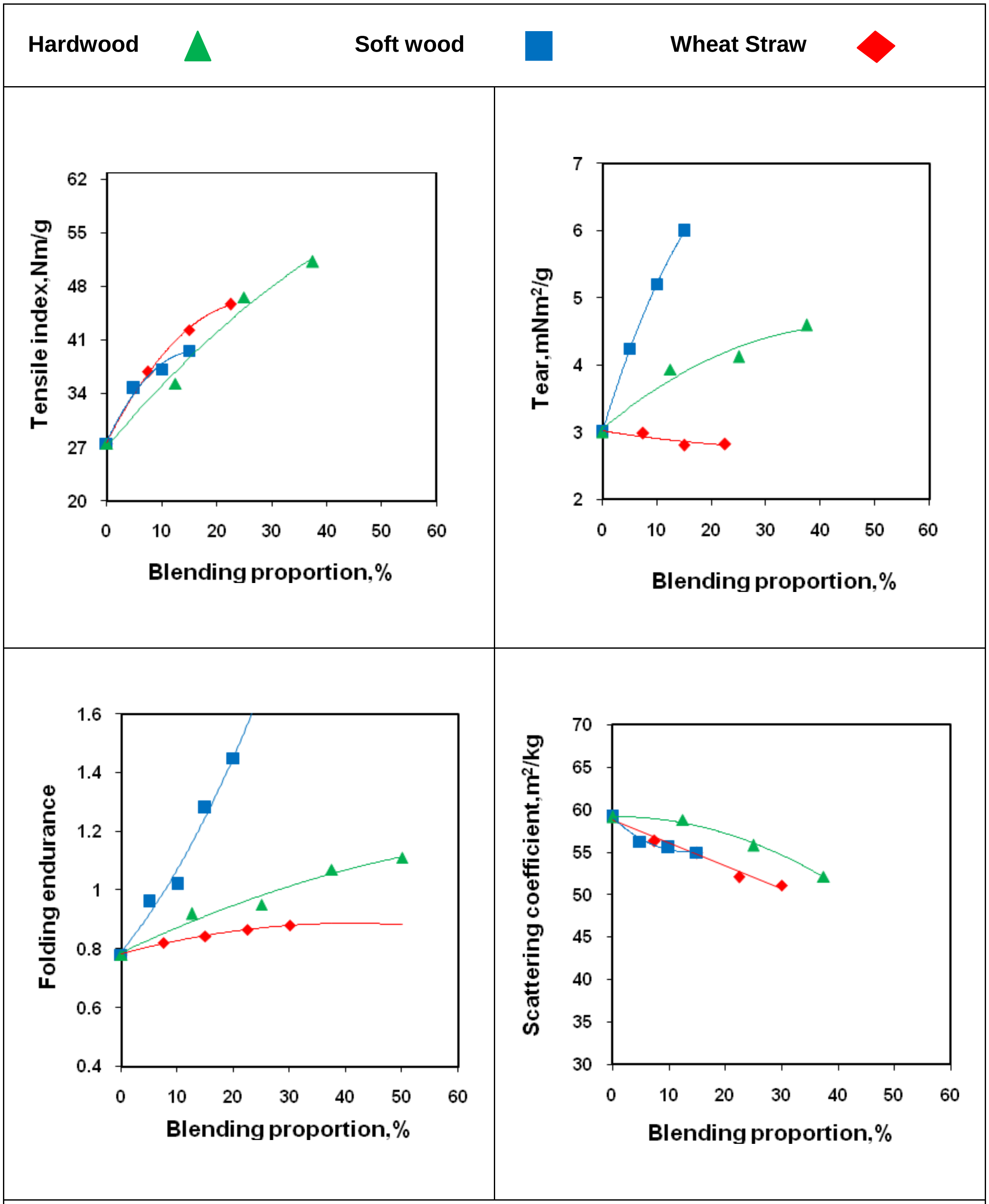


Fig. 4. Effect of Blending of different pulps with bagasse pulp having 15% calcium carbonate loading by *in-situ* precipitation on Strength properties of the handsheets at different proportion levels

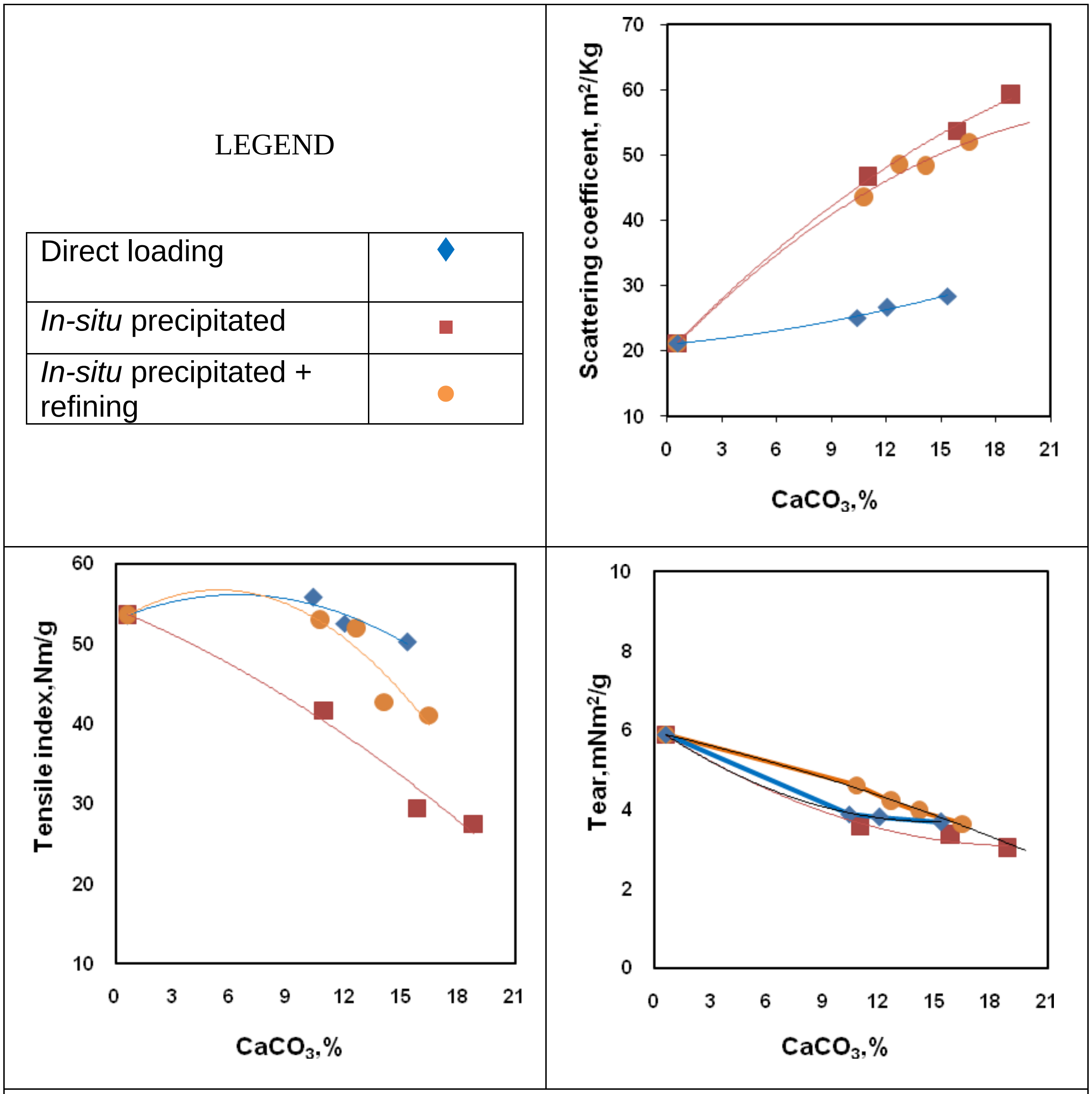


Fig. 5. Effect of filler on Strength properties of *in-situ* precipitated plus refined bagasse handsheets and *in-situ* precipitated with carbon dioxide gas at different $CaCO_3$ levels

CONCLUSIONS

1. Precipitation of calcium carbonate by adding calcium hydroxide solution to bagasse pulp that had been soaked with sodium carbonate solution resulted in a large proportion of the precipitated particles being located in the fiber lumen.
2. *In-situ* precipitation of calcium carbonate on bagasse fibers resulted in a very significant increase in specific scattering coefficient and consequently large improvements in opacity and brightness of the handsheets made of such pulp.

3. At the same level of filler loading, the scattering coefficient of *in-situ* precipitated pulp was much greater than that of the directly loaded pulp.
4. *In-situ* precipitation of calcium carbonate caused a drop in strength properties of bagasse pulp. This drop in properties was less than the drop caused by the direct filler loading, when compared at equal ash level.
5. The strength properties of *in-situ* precipitated bagasse pulp could be improved by blending with other pulps, with some reduction in scattering coefficient. The furnish may be optimized for strength and optical properties.
6. The strength properties of *in-situ* precipitated bagasse pulp could also be improved by refining the *in-situ* precipitated bagasse pulp once again.
7. The effect of *in-situ* precipitation of calcium carbonate on pulp fibers was quite different for bagasse pulp for hardwood pulp. *In-situ* precipitation of calcium carbonate on hardwood fibers neither showed much improvement in optical properties nor much reduction in strength properties.

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