FIBER LOADING OF HARDWOOD PULP BY IN-SITU PRECIPITATION OF ALUMINOSILICATE

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Sodium aluminosilicate has been precipitated in-situ as filler on hard-wood bleached kraft pulp fibers using papermaker's alum and sodium silicate. The filler was produced in two ways, first in the absence of the fibers and second in the presence of fibers, i.e. in-situ precipitation of filler. The filler produced in absence of fiber was then added to the pulp slurry. Various pulp and paper properties were compared for direct loading of market filler, fresh filler loading, and filler prepared in-situ with fibers. In-situ precipitation technology provided paper with significant improvements in various properties of paper as compared to fillers directly added to the stock. Bulk and stiffness of the handsheets prepared with in-situ precipitation were much higher as compared to those of sheets prepared with fillers directly added to the pulp. There was no appreciable increase in brightness and whiteness of paper with in-situ precipitation, as an appreciable proportion of filler was precipitated inside the fibers. In-situ filler loaded pulps showed a higher filler retention value as compared to directly filler loaded pulps, as a high dose of retention aid was needed with the fillers directly added to the stock.

Keywords: Lumen loading, Aluminosilicate, Eucalyptus pulp, Stiffness, Bulk

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INTRODUCTION

For some applications of paper, its strength, stiffness, and bulk become the critical properties. Using more filler in paper can increase opacity, but this usually decreases paper strength and stiffness (Bown, 1985). Thus, paper structure should be altered in such a way that desirable paper properties are maintained. Both pigments and cellulosic materials need to be used effectively in order to achieve the desired properties at increased levels of filler. New developments such as precipitated fillers and pigments are known to offer new opportunities to improve paper properties. Improved information on synergism and interaction of precipitated pigments with fibers and fines may provide papermakers with new ways to improve paper properties. It has also been assumed that inorganic salts precipitated within fiber walls may increase fiber stiffness, with some impact also on light scattering and paper stiffness (Silenius, 1996).

The tradition method of adding mineral content to paper can be described as direct filler loading. In comparison to the traditional approach, fiber-loading technology may offer a new route to improve strength of paper, formation, and retention (Klungness *et al.*, 1996) simultaneously, since filler retention may be less dependent upon chemical

retention, flocculation, and agglomeration. The studies on filler-loading show that the filler can be incorporated onto or within fibers by three different ways: i) the direct loading of filler with fibers - presently used in most of the pulp and paper industries, ii) lumen loading of softwood fibers by mechanical diffusion of filler into fiber lumens through pit apertures (Middleton *et al.*, 2003), and iii) lumen and/or cell wall loading by in-situ precipitation of filler (Siven and Manner, 2003).

Incorporating fillers inside fibers has been extensively studied, not only as a means of achieving better filler retention but also for better paper properties (Green *et al*., 1982; Middleton *et al.,* 2003; Miller and Paliwal, 1985; Petlicki and van de Ven, 1994). The in-situ precipitation in the fiber can either be within the cell wall or within the lumen. Many investigators have reported that fiber wall filled paper exhibits greater tensile, burst, and tear strength than corresponding conventional paper. The better strength that is observed is assumed to be due to increased hydrogen bonding of fibers, because the filler is located inside the fibers (Green *et al*., 1982; Miller and Paliwal, 1985; Allan *et al*., 1992). In summary, methods of incorporating fillers inside fibers can be based on precipitation, or filler can be mechanically stirred with pulp slurry, transferring filler into the fiber lumen. In precipitation, the approach has usually been to saturate pulp fibers with a soluble salt and to precipitate filler by another soluble salt. Fiber loading using an aluminum compound for improving the physical strength properties has been reported by Siven and Manner (Siven and Manner, 2003). However, published information related to the effects of in-situ precipitation of filler inside hardwood fibers is limited, and issues related to bulk and bending stiffness have not received sufficient attention.

The present study deals with the effects of in-situ precipitation of aluminosilicate within bleached hardwood kraft pulp on handsheet properties including bulk, bending stiffness, and other strength and optical properties.

EXPERIMENTAL

Materials

A never dried bleached kraft pulp obtained from an integrated pulp and paper mill in north India using hardwoods (mainly 50% eucalyptus and 50% poplar) was used in this study. The beating of pulp was done in a PFI mill (Hamjern Maskin A/S, Hamar, Norway; PFI mill no. 616) to achieve 420 mL CSF value. Fresh sodium alumino-silicate was prepared in two different ways, i) precipitation in absence of fibers, and ii) in-situ precipitation (in presence of fibers). Commercial grade sodium silicate and papermaker's alum were collected from indigenous sources.

In-situ Precipitation of SAS

In-situ precipitation of sodium aluminosilicate (SAS, i.e. precipitation in presence of fibers, SAS-ISP) was done as per the following procedure. A fixed amount of 44% aluminum sulfate-14 hydrate (alum) solution was impregnated into the never dried beaten pulp of 5% consistency. The mixing of this slurry was done for about 10 minutes in a high-speed disintegrator at room temperature (around 26 ^{o}C) so that the fiber lumen and cell wall are saturated with the ionic solution. Thereafter, sodium silicate of 35%

concentration was added gradually, over about 15 minutes, to the impregnated pulp slurry while stirring. The optimum end pH was 7.5-7.8. The slurry was further agitated for 10 minutes to allow the surface to become saturated with mineral. To determine the actual amount of filler precipitated within the fiber, the pulp was washed in a Bauer McNett classifier to remove the excess filler that either was not attached or attached loosely to the outer surfaces of the fibers. The general process steps involved in this process are depicted in Fig. 1. Sodium alumino-silicate in absence of fibers was also prepared in a similar manner as described above.

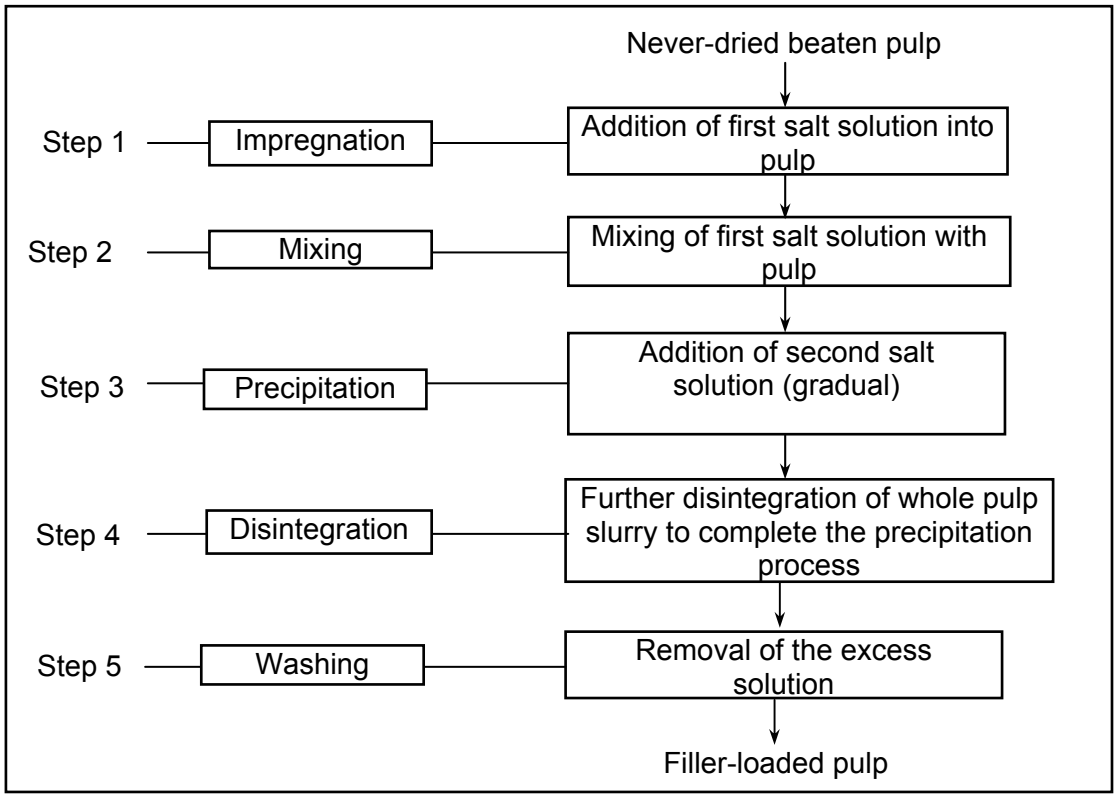

Fig. 1: General process steps for SAS-ISP

Direct Filler Loading

The fillers added directly to the pulp slurry were Hydrex-P® (Na-Mg alumino-silicate from Huber Corporation) and Finex (talc - magnesium silicate from a local supplier) in the form of slurry having 20% solids. The freshly prepared sodium alumino-silicate (SAS) was also added directly in the pulp. The retention aid (Percol-47® of CIBA Specialty Chemicals) was used with Na-Mg aluminosilicate and freshly prepared SAS to achieve good first pass ash retention. Paper hand sheets were prepared at 2.5, 5.0, and 7.5% ash levels with all fillers.

Preparation of Handsheets

Paper handsheets having a basis weight of 70 g/m^2 were prepared for all of the experiments. In the case of SAS-ISP, sheets were prepared without washing of pulp in

Baur McNett classifier (as such precipitated filler and fibers). This slurry consisted of both fiber loaded filler as well as filler outside fibers. The properties of handsheets formed by in-situ precipitated sodium alumino-silicate (SAS-ISP) were compared to those of directly added fillers i.e., SAS, Na-Mg aluminosilicate and talc.

Analytical Techniques

The physical properties of the handsheets were determined according to relevant standard methods. The optical properties were tested on a Datacolor brightness tester (Datacolor, USA; model: Spectraflash 300 UV) brightness tester. Ash in the paper was estimated according to TAPPI Test Method T-211 om-93 by the incineration of paper at 575±25 ^{o}C in a muffle furnace. First pass ash retention was calculated from the ash content in the stock and that in the white water. Particle size of filler was determined using 10% slurry in a Particle Size Analyzer (Microscan II from Quantachrome Corporation, USA).

All of the experiments were performed in duplicate and repeated once more to confirm the results and observations of the earlier set. The average values of all of the parameters for 95% confidence limits, from up to four replicates, were calculated and reported herewith.

RESULTS AND DISCUSSION

The physical properties of different fillers used in this study are presented in Table 1. The brightness and whiteness of Na-Mg aluminosilicate were the highest. SAS was the finest filler, having around 87.3% of the particles less than 2-µm.

Table 1. Physical Properties of Different Fillers

Parameter	Talc	Na-Mg aluminosilicate	SAS
Brightness (%ISO)	93.5	99.2	96.3
CIE Whiteness	94.2	101.7	94.9
Particles < 2 µm (%)	20.0	78.0	87.3
pH	9.21	9.70	7.22

The actual amount of SAS precipitated within the fiber was determined by thoroughly washing the pulp in the Bauer McNett classifier after the complete process of in-situ precipitation of aluminosilicate. During the process of washing (in the Bauer McNett device), the fines were removed, which also carried away the SAS precipitates outside the fiber. Unwashed and washed pulps were also examined under the microscope to see the location of the precipitated alumino-silicate. The unwashed pulp showed precipitated material at the outer surface of the fiber, whereas the washed pulp was totally free from outside precipitate. The ash in the pulp was found to decrease as a consequence of washing. This trend was seen at all the ash levels (Table 2). The ash content of the pulp after washing corresponds to the filler (ash) inside the fiber.

Table 2. Ash Contents in Pulp

Sr. No.	Ash in pulp (%)	
	Before Washing (in Bauer McNett)	After Washing (in Bauer McNett)
1	4.0	1.8
2	5.5	2.1
3	7.1	2.6
4	10.1	3.0

First pass ash retention (FPAR) of SAS-ISP was the highest, as expected based on the information from the literature. This was attributed to the precipitation of some amount of the filler inside the fibers. The same trend could be seen at all the ash levels (Fig. 2). The FPAR of talc was also relatively high, which is attributed to its larger particle size. The higher FPAR value provides a cleaner white water system. Therefore, in the case of SAS-ISP, the white water system would be expected to be cleaner in comparison to the white water system of directly filler-loaded pulps.

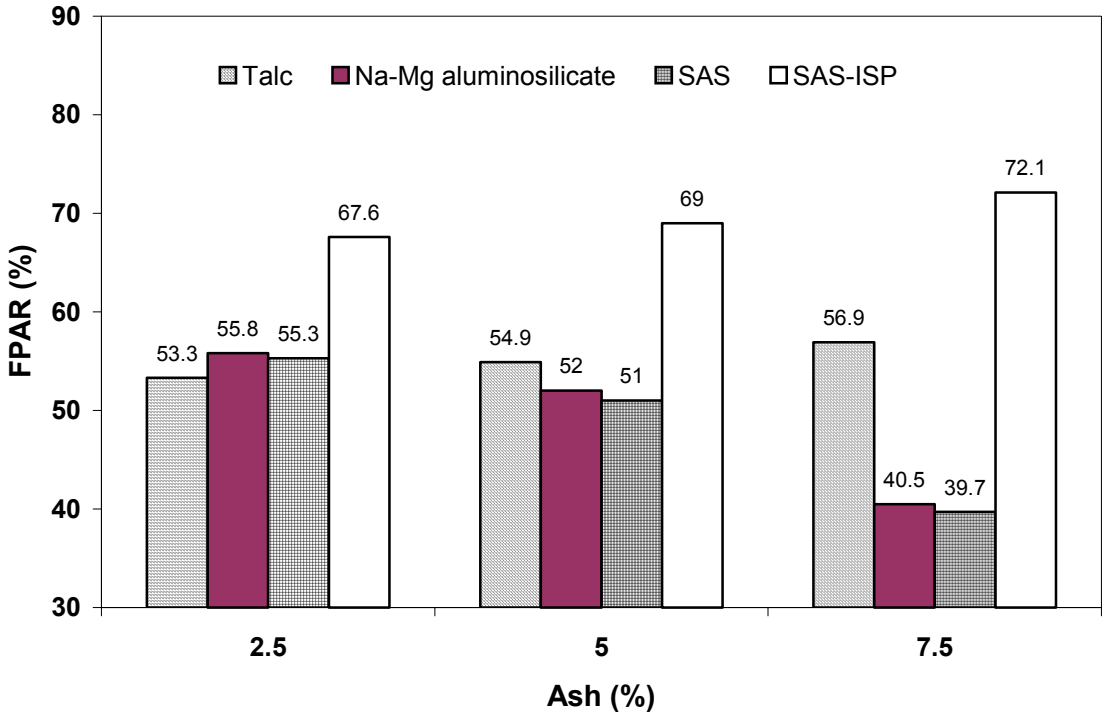

Fig. 2. Effect of filler on first pass ash retention (FPAR) at different ash levels

Normally, paper's bulk decreases with increasing ash content. From Fig. 3, it can be seen that the bulk also depended on the type of filler used. In some cases it decreased, whereas in others it increased. The bulk of paper decreased in case of talc, whereas in case of Na-Mg aluminosilicate and SAS it increased as compared with the blank. This difference in behavior may be due to the bulk density of the fillers. The bulk in case of SAS-ISP increased appreciably, probably due to some precipitation of filler inside the

fibers, which decreased the collapsibility of fibers, resulting in increased thickness of the paper. From these results, it is confirmed that some of the filler had been precipitated within the fiber in the case of SAS-ISP. The SAS filler precipitated inside the fiber could be either in the fiber lumen or in the fiber wall or in both. However, no such differentiation could be made in this study.

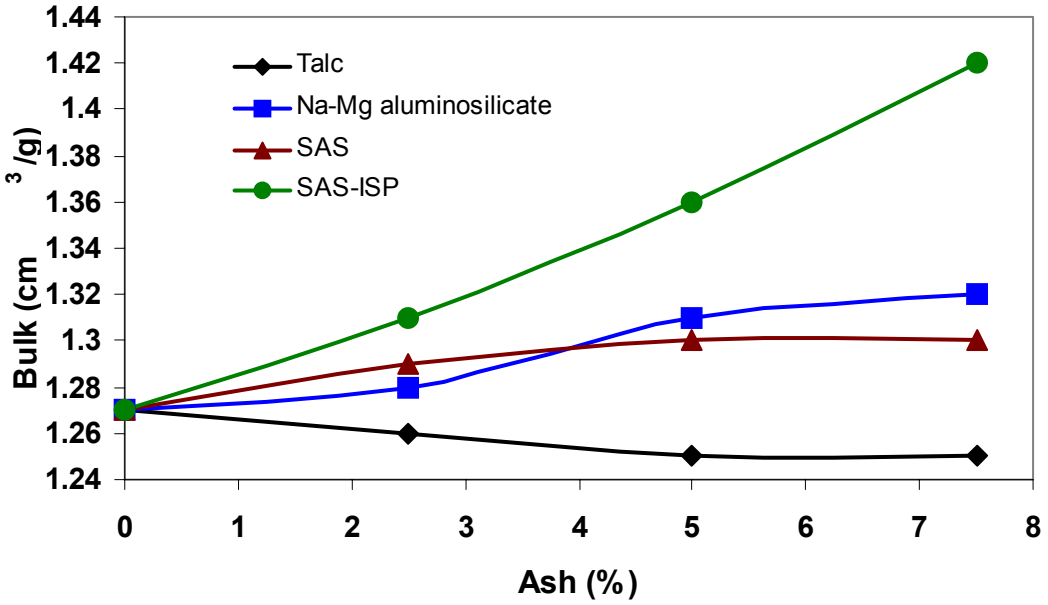

Fig. 3. Effect of ash content on bulk with different fillers

The bending stiffness normally decreases with increase in filler loading. In fact, bending stiffness of paper depends upon the elastic modulus of the fibers and the thickness of the paper. With increase in thickness, stiffness increases. It can be seen from Fig. 4 that the bending stiffness (L&W stiffness) of paper handsheets was highest in case of SAS-ISP, as compared to that of direct filler-loaded sheets. The elastic modulus of the fiber is expected to increase with the fiber loading due to gluing effect of the mineral precipitate and the thickness of the fiber will increase due to non-collapsibility of the fiber on getting filled with the precipitate. Thus, the bending of individual fiber is affected by the same, resulting in high values of bending stiffness of the paper. Initially, the stiffness increased and afterwards decreased slightly with increasing ash level (Fig. 4) due to precipitation of aluminosilcate on the outer surface after certain ash levels.

All of the physical strength properties decreased to a large extent with direct loading of fillers, whereas in the case of SAS-ISP, all of the strength properties were on the higher side as compared with direct filler loading. The breaking length decreased with the addition of filler in all the cases (Fig. 5). The extent of drop in breaking length was much lower in the case of SAS-ISP as compared with direct filler loading.

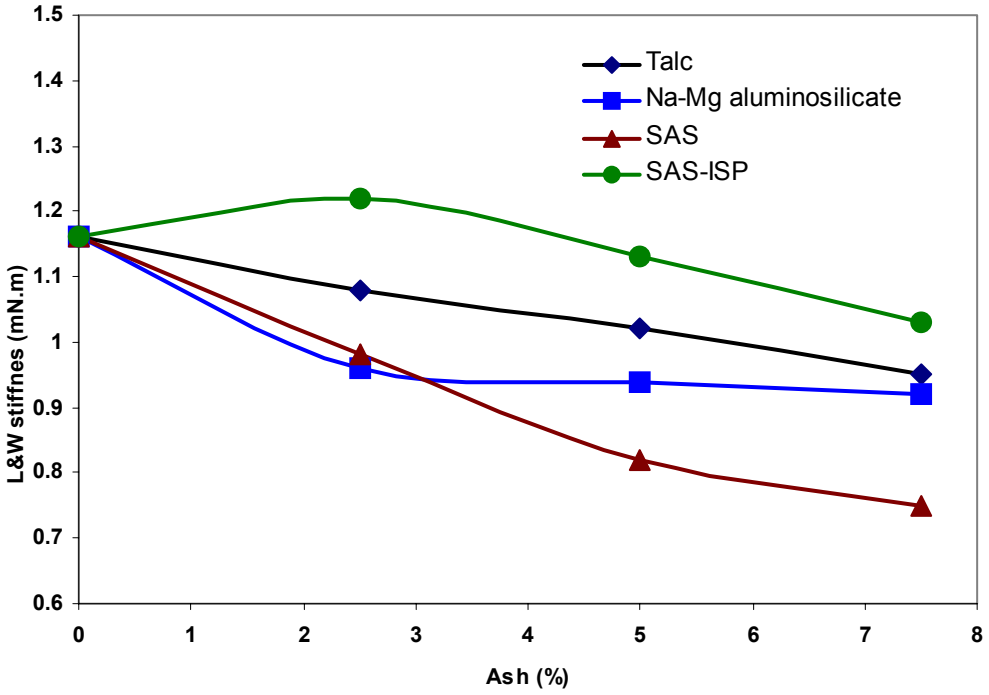

Fig. 4. Effect of ash content on stiffness with different fillers

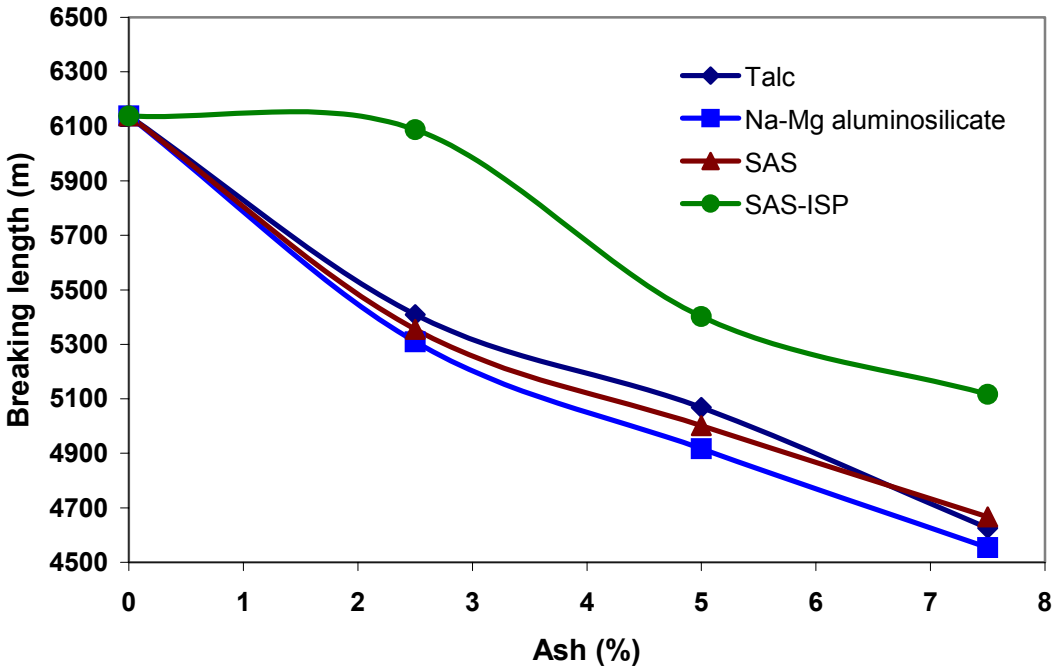

Fig. 5. Effect of ash content on breaking length with different fillers

The smallest size filler had the most detrimental effect on paper strength. A good indication of the role of particle size is that the loss of burst index increases with the total surface area of fillers (Li *et al.,* 2002). From Fig. 6, it can be seen that the burst index of paper handsheets decreased with increase in ash level in all the cases. However, the loss in burst index was much lower in the case of SAS-ISP as compared with direct filler loading. The highest loss was seen in case of Na-Mg aluminosilicate, followed by SAS and talc, in order of increasing particle size (refer Table 1).

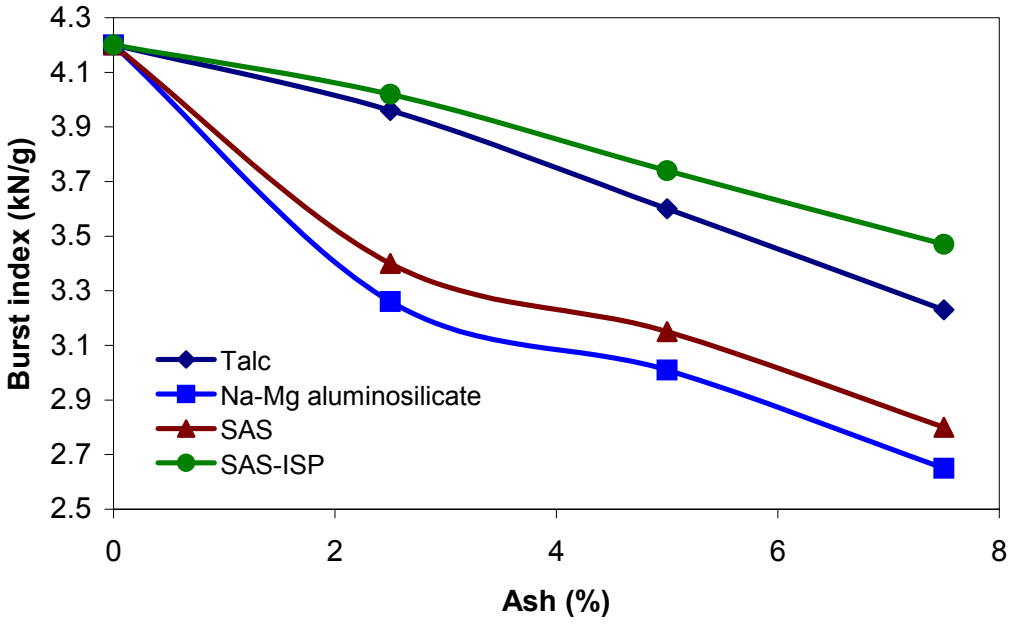

Fig. 6. Effect of ash content on burst index with different fillers

In case of direct filler loading, the tear index of paper handsheets decreased with addition of filler (Fig.7). The trend of decrease in tear index was different for different fillers. It was highest in case of Na-Mg aluminosilicate, followed by SAS and talc, whereas in case of SAS-ISP, this trend was the opposite. There was an increase in tear index with increase in ash content. This increase may be because of an increase in the fiber thickness on filling of fiber with SAS precipitate, so that the force required to tear the sheet increased.

The internal bond strength (Scott bond) of paper hand sheets prepared with direct filler-loaded pulp in comparison to the blank decreased with increase in ash level, whereas it slightly increased in the case of SAS-ISP (Fig. 8). Often, the Scott bond value for a paper has a strong positive correlation with the tensile strength, however this unusual behavior for SAS-ISP sheets supports the assumption that an appreciable portion of the filler precipitated inside the fiber lumen.

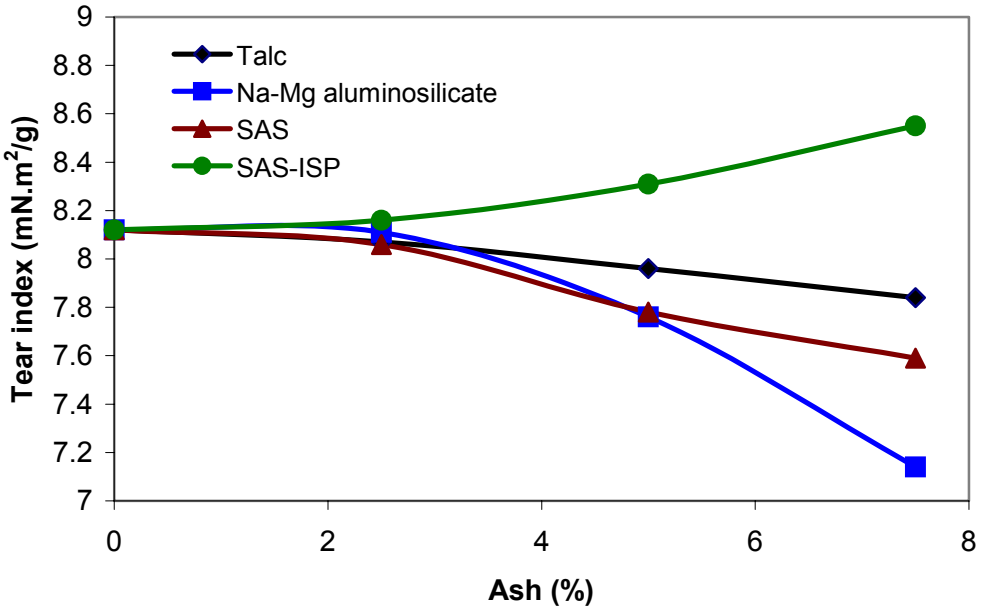

Fig. 7. Effect of filler on tear index at different ash levels

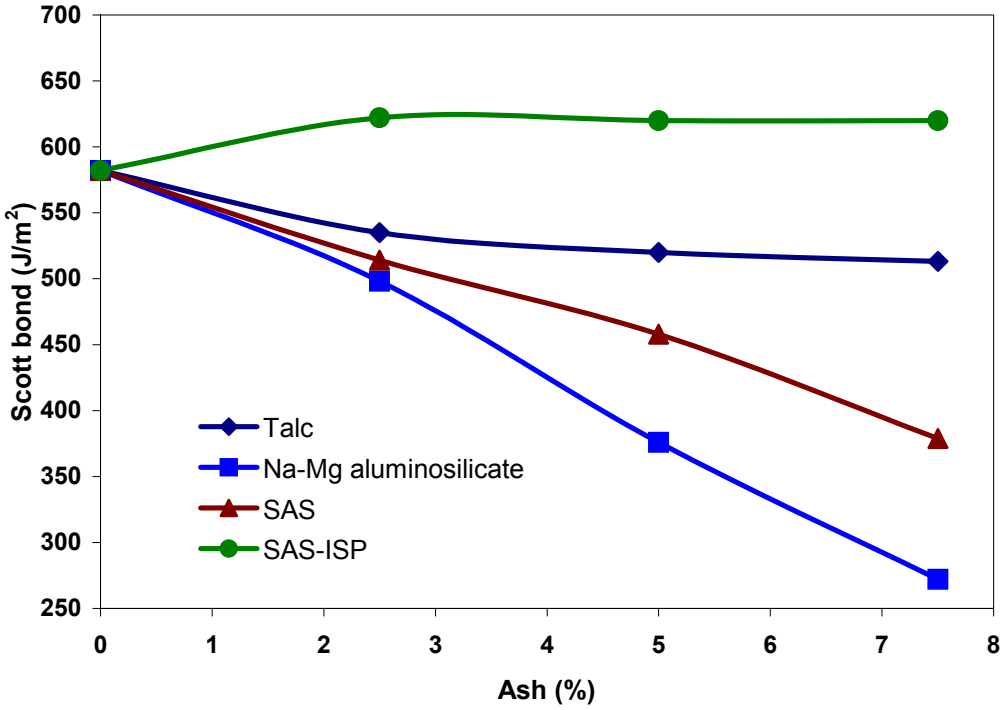

Fig. 8. Effect of filler on Scot bond value at different ash levels

While a tensile tester measures the tensile force required to rupture a sheet, the Scott bond tester measures the energy required to rupture the sheet in the thickness-direction. The increased precipitation of filler inside the fiber should decrease the intra-fiber bonding and it is likely that an increased number of partial breakages within fibers take place before delamination of the sheet occurs, adding to the increased Scott bond test value for SAS-ISP sheets. In addition, the internal bond strength is sensitive to any non-uniformity or layering in the thickness direction since delamination will occur at the weakest plane. The weakest location depends on the z-directional distribution of fines and fillers, and the bonding degree. It seems that the filler precipitated outside the fiber in case of SAS-ISP at higher ash content, reduces the no-uniformity across the thickness direction of the paper sheet though it might reduce the inter-fiber bonding area, resulting in no drop in internal bond strength. Whereas for direct filler-loaded sheets, the filler tends to reduce the inter-fiber bonding area; the finer the filler the greater is the interference with the fiber bonding and probably non-uniformity across the thickness.

Values of all the optical properties were lowest in the case of SAS-ISP as compared with direct filler loading (Fig. 9, 10). In fact, a major portion of the SAS-ISP was precipitated inside the fibers, and it was not affecting the reflectance or scattering of light to the same extent as direct SAS addition. In case of direct filler loading, the filler seemed to have more direct interaction with the light, hence there was more reflection of light. The highest brightness was achieved in the case of sheets prepared with Na-Mg aluminosilicate (Fig. 9) because of the small particle size and high brightness of this filler as shown in Table 1.

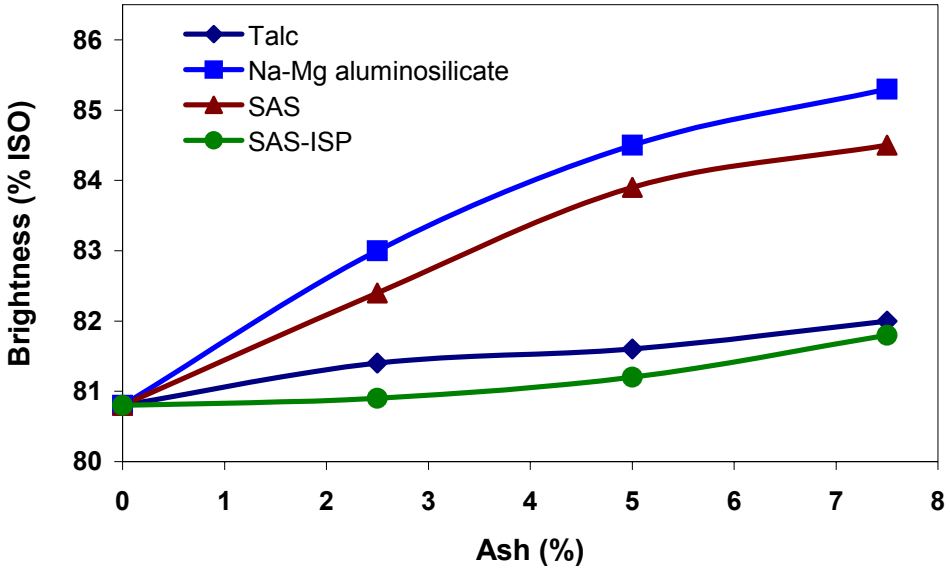

Fig. 9. Effect of filler on brightness as a function of ash content

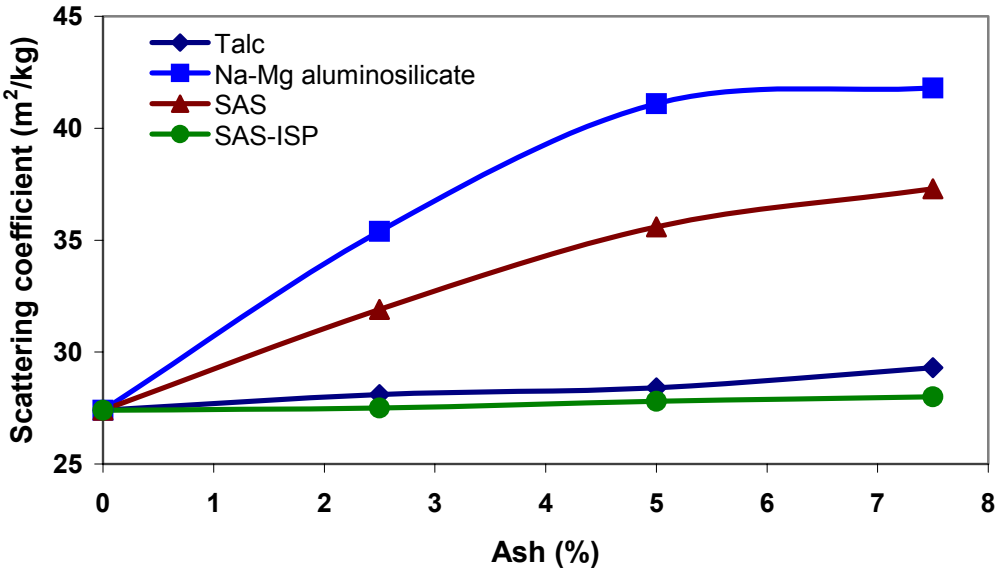

Fig. 10. Effect of filler on scattering coefficient as a function of ash content

The freshly prepared SAS was also providing good brightness, as compared with other fillers. When the comparison was made between SAS and SAS-ISP (i.e. as such filler preparation in absence of fibers and in-situ precipitation of filler in presence of fibers respectively), it was seen that the brightness of paper in case of SAS-ISP was quite low. The scattering coefficient was also quite low in case of SAS-ISP as compared with direct filler loading (Fig. 10) since appreciable portion of the filler got precipitated inside the fiber, which was not affecting the light scattering. The highest scattering was observed with Na-Mg aluminosilicate, presumably due to its having the smallest particle size.

CONCLUSIONS

Sodium aluminosilicate (SAS) has been precipitated in-situ as a filler inside the fibers. From this study, the following conclusions can be drawn. The amount of SAS precipitate inside the fiber did not increase in the same proportion as of total SAS precipitate (ash content); after a certain level, precipitation took place mainly at the outer surface of the fiber. In the case of freshly prepared SAS added directly to the pulp, strength properties of paper were slightly on the higher side as compared to those of Na-Mg aluminosilicate. Bulk and bending stiffness of handsheets prepared with SAS-ISP were much higher as compared to that of sheets prepared with fillers added directly to the pulp. All the strength properties were higher in case of SAS-ISP as compared to those of direct filler loading. There was no appreciable increase in brightness and scattering coefficient of paper with SAS-ISP, as the filler appeared to be retained in the fiber (within the lumen or within the fiber wall).

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