

# THE DRY STRENGTHENING EFFECT OF CATIONIC STARCH WET-END ADDITION ON FILLED PAPERS

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## ABSTRACT

The effects of cationic starch wet-end addition on the mechanical and optical properties of clay loaded papers are discussed. It is shown that massive strength improvements can be achieved at high filler loadings with high starch additions. The properties of super-filled paper structures with filler loadings up to 90% are also reported. Cationic starch wet-end addition is superior to starch impregnation applications (e.g. size press) on highly filled structures. This behaviour is understood from the effect of wet-end starch addition on sheet consolidation (sheet density improvement). Wet-end starch addition increases the drying stress built up during sheet consolidation. This increase is generally much higher for filled papers than for papers of zero filler content.

The effects of fillers and wet-end starch addition on the intensity of stress concentrations in paper structures have also been investigated. It was found that an increase in filler level increases the stress concentration, whereas starch addition leads to a decrease. Addition of starch may actually bring the stress concentration intensity in a highly loaded sheet down to the level of a sheet with no filler at all. On the basis of the results, a mechanism of lubrication by which wet-end cationic starch addition improves the strength properties of filled papers is proposed.

## INTRODUCTION

Although the use of starch as a papermaking additive predates the invention of the Fourdrinier machine and many reviews (see e.g. 1-3) are available, little systematic information is generally available on the effects of wet-end starches on the properties of filled papers. In a recent publication from this laboratory (4) the effects of cationic starch wet-end addition on the properties of clay-filled papers were reported. It was shown that massive strength improvement can be obtained at high addition levels of cationic starch on highly filled papers.

In general there are two principally different ways of adding starch to a paper sheet. The starch may be added either at the wet end or in a size press. In the former case the starch is present during sheet consolidation, whereas in the latter case the starch is added to a consolidated sheet. Our accumulated experience indicates that the large relative strength improvements obtained by the wet-end addition of starch to highly filled papers depend not only on the fact that a high filler content gives a weak paper structure if no dry strength agent is added but also on a positive effect of cationic starch wet-end addition on the consolidation process of highly filled papers. Therefore it is of interest to compare wet-end addition with the impregnation addition of starches to unfilled and filled papers. One of the objects of this paper is to report the results of such a comparison.

Besides summarizing some of our previous findings together with this latter aspect, the major object of this paper is to present and discuss a hypothesis for the mechanism of action of hydrophilic mucilages, of which starch is an example, on the properties of filled papers. The hypothesis, which is necessarily in an evolutionary stage of development, emphasises the lubricating action of the mucilage during sheet consolidation.

## EXPERIMENTAL

### Materials

Unless otherwise stated, the pulps used in the experiments were commercially available pine and birch bleached kraft pulps supplied in dry lap form. After disintegration, the pulps were beaten to about 20° SR and subsequently washed on a Buchner funnel prior to use.

The cationic starch (CS) used in this investigation was a quaternized potato starch (Posamyl E, AB Stadex, Sweden, DS = 0.03). The anionic polyacrylamide (A-PAM) used was a copolymer from sodium acrylate (32.5 mole %) and 67.5% acrylamide (Percol 155, Allied Colloids, Bradford, U.K.). The quantities of A-PAM and CS added refer in all cases to the dry polymer. Stock solutions of A-PAM were made by dissolving 1g in 1000ml deionized water with magnetic stirring for 12 hours. The CS was gelatinized at 90°C for 10 min at a concentration of 1% in deionized water. The polymer solutions were stored for no more than 48 hours.

The clay used was of a common filler grade type (Grade C, ECC, UK; BET surface area =  $8\text{m}^2/\text{g}$ ; 45% < 2  $\mu\text{m}$ ). The clay slurries were dispersed with the aid of 0.3% sodium hexametaphosphate (Calgon, Svenska Hoechst). The clay content in the sheets is always expressed as the mass fraction of the total mass of the sheets.

### Methods

After the pulp had been mixed with the clay dispersion, the mixture was diluted with tap water to a stock consistency of 3 g/l. the pH of this stock was approximately  $8.0 \pm 0.2$  and was not further adjusted. The retention of CS was aided by the addition of A-PAM five minutes after the CS. The sheet was then formed after a further ten minutes. Sheets with a nominal grammage of  $85\text{g}/\text{m}^2$  were formed on a dynamic sheetformer (Formette Dynamique, CTP, France) which was set to give a tensile strength anisotropy between 3 and 3.5. This dynamic former gives a high filler retention even without retention aid

addition. Indeed, sheet formation is generally superior to that of conventional hand-sheets or machine-made sheets. Thus, the effects of sheet formation and selective retention of certain clay fractions on the strength and optical properties of the sheets are believed to be of minor importance. The sheets were then pressed in a double-felted laboratory press between two cylindrical rolls. After pressing, the sheets were dried under biaxial restraint in special drying frames (5). The strength and optical properties were tested according to standard methods. The amount of CS retained on the stock was measured by determining the residual amount of CS in solution after filtration of the stock on a glass fiber filter (Whatman GF/A). The starch concentration was determined using the phenol-sulphuric acid colometric method (6). The retention of CS was always greater than 95%.

The development of stress during drying under uniaxial restraint was measured using a specially designed drying frame. The frame was equipped with a load cell so that the drying force could be determined. During measurements the frame was placed on an electronic balance which was capable of handling the total weight of the frame as tare weight, thereby facilitating the monitoring of sheet weight. The 100mm wide sheet was held between heated clamps of sintered metal that were controlled to keep the clamped ends of the sheet slightly drier than the remaining portion of the specimen during the process of drying. The free span between clamps was 160mm. Drying was accomplished with the application of infrared radiation, totally 1 kW on each side of the sheet, and the water evaporated was continuously removed with the aid of a small electric fan. During drying, the sheet reaches a temperature corresponding to a quasi-wet-bulb temperature (cf. Ref 8) of about 50°C. After the water is dried out, the temperature immediately increases to around 100°C.

A measure of the stress intensity in the sheets was obtained from creep rupture measurements. The time to creep rupture was determined under various tensile loads with the use of a simple apparatus where, upon rupture of the specimen, a weight carried by a specimen fell onto a

microswitch which stopped an electric timer showing the time to rupture of the specimen. From a plot of the logarithm of time to rupture versus applied load, a stress intensification factor was calculated using the semi-empirical formula of Zhurkov (7):

$$t_f = t_0 \cdot \exp \left[ \frac{U_0 - j \cdot \sigma / \rho}{RT} \right] \quad (1)$$

where

$t_f$  = time to failure

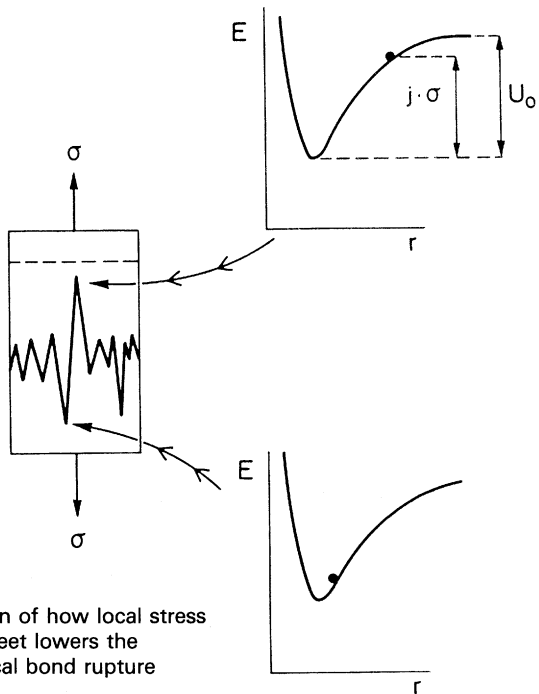
$t_0$  = empirical constant related to the time of an atomic vibration  $\approx 10^{-13}$ s.

$U_0$  = activation energy for bond rupture (kJ/mol)

$\sigma$  = the stress ( $\text{N/m}^2$ ) to which the sample is subjected

$j$  = stress concentration factor  $\frac{\text{kJ}}{\text{mol}} \cdot \frac{\text{kg}}{\text{MN}\cdot\text{m}}$

$\rho$  = sheet density ( $\text{kg/m}^3$ )



**Fig 1**—Schematic illustration of how local stress concentration in a paper sheet lowers the activation energy  $U_0$  for local bond rupture

The physical basis of this formula is simple and is illustrated in Fig. 1. If a sheet of paper is subjected to a certain stress level the activation energy for bond rupture is decreased in regions with a high stress concentration by the factor  $j$ , proportional to the average stress level in the material. Thus, local yielding will occur in regions with a high stress concentration. If the time to failure of paper strips under different tensions is recorded, the stress concentration factor  $j$  can be determined and this gives a measure of the intensity of stress concentrations in the paper sheet.

## RESULTS

### The Effects of Cationic Starch Wet-End Addition on Paper Properties

In a previous communication (4) it was reported that the strength properties of filled papers can be improved considerable by adding large quantities of cationic starch. In Table 1 some of these data illustrating the major features have been compiled for a paper stock composed of 50% bleached softwood kraft pulp, 50% bleached hardwood kraft pulp and different amounts of filler clay. The effects of a high addition of cationic starch (CS) on the properties of sheets containing no filler and 50% clay can be compared. The important feature is that the relative effect on the strength properties of adding CS is much more accentuated on highly filled sheets. For an unfilled sheet the tensile index increased from 52 to 79.5 kNm/kg, whereas for a sheet with 50% clay the tensile index increased from 10 to 35 kNm/kg, i.e. by 250%. This effect is even more accentuated if the tensile stiffness index values are compared. It is difficult to improve the tensile stiffness index for unfilled sheets whereas a massive improvement is obtained for highly filled papers. The light scattering coefficient deteriorated, however, when CS was added.

It may also be noted that the density of sheets made under identical conditions is higher when CS is added, especially for highly filled sheets. This effect is shown in Fig. 2 where the apparent sheet density is given versus clay content for two levels of CS addition. This illustrates that the sheet consolidation is improved when wet-end addition of CS is employed.

Clay content %	Starch addition %	Tensile index kNm/kg	Tensile stiffn index MNm/kg	Bending stiffn index Nm <sup>7</sup> /kg <sup>3</sup>	Strain to failure %	Light scatt coeff m <sup>2</sup> /kg	Density kg/m <sup>3</sup>
0	-	52	6.4	1.02	2.1	34	560
0	4.2	79.5	7.3	1.33	3.2	31	568
15	-	30	4.6	0.82	1.5	44	580
50	-	10	2.0	0.24	1.0	66	655
50	4.2	35	5.7	0.50	1.6	58	720

Table 1. The effect of wet-end cationic starch addition on paper properties.

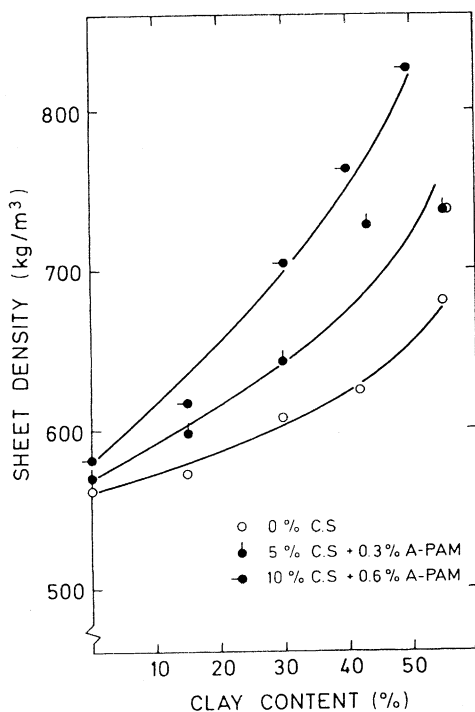


Fig 2—The effect of cationic starch wet-end addition on the apparent sheet density for clay-filled papers

### Super-Filled Paper Sheets

The massive strength improvements obtained at high filler loadings suggested an investigation of the properties of super-filled paper sheets with high wet-end additions of CS. Such paper sheets were made from bleached softwood kraft pulp with different amounts of clay up to a content of 90%. The properties of these papers are tabulated in Table 2. It can be noted that if CS is added the bending stiffness index  $S_b/w^3$  does not decrease at high filler contents where a drastic decrease would otherwise be expected. A sheet with a filler content of 90% with 5% CS and 0.3% A-PAM added has a higher bending stiffness than a paper with 60% clay without any added CS.

Clay content %	Starch addition %	Tensile index kNm/kg	Tensile stiffn index MNm/kg	Bending stiffn index Nm <sup>7</sup> /kg <sup>3</sup>	Strain to failure %	Light scatt coeff m <sup>2</sup> /kg	Density kg/m <sup>3</sup>
60	-	10	2.2	0.2	1.1	76	805
60	5	33	5.7	0.4	1.6	67	881
70	-	6	1.4	0.1	1.0	79	855
70	5	22	5.1	0.3	1.2	74	903
80	5	13	4.3	0.3	0.8	83	889
90	5	7	3.7	0.3	0.4	86	859

Table 2. Properties of super-filled paper sheets with and without dry strength additives.

The density increases markedly with increasing filler content at lower clay contents, but this is not the case at these higher filler addition levels. In fact, there was a slight decrease in density, according to the SCAN standard method, at very high filler contents (see Table 2).

Sheet without added starch have a soft and silky feeling at filler contents over 60%, whereas a sheet with added starch and a filler content of 90% still has "rattle". Interestingly these superfilled papers have the subjective character of being a sheet of paper, at least below a filler content of 85%.



Figure 3 shows a cross-section of a paper sheet composed of 80% clay, 15% fibers and 5% cationic starch. It is obvious that the sheet structure is highly densified and essentially free from large voids.

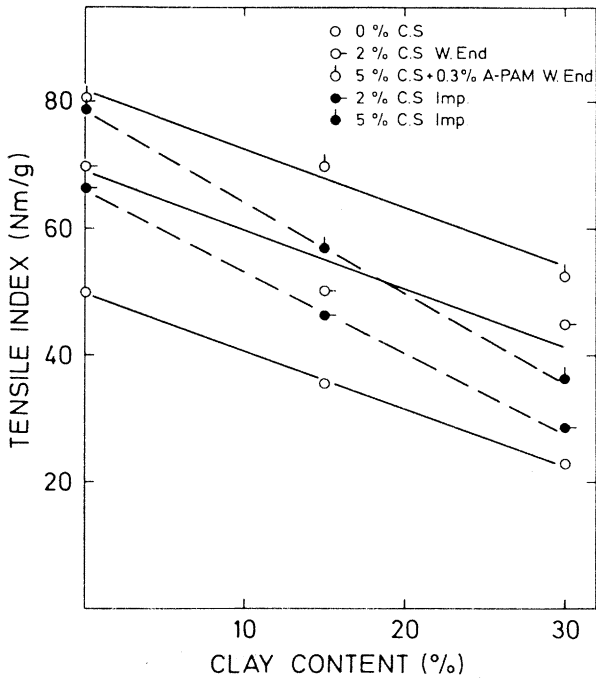


**Fig 3**—Cross-section of a paper sheet composed of 80% clay, 15% bleached softwood kraft fibre with 4.2% cationic starch and 0.3% anionic polyacrylamide

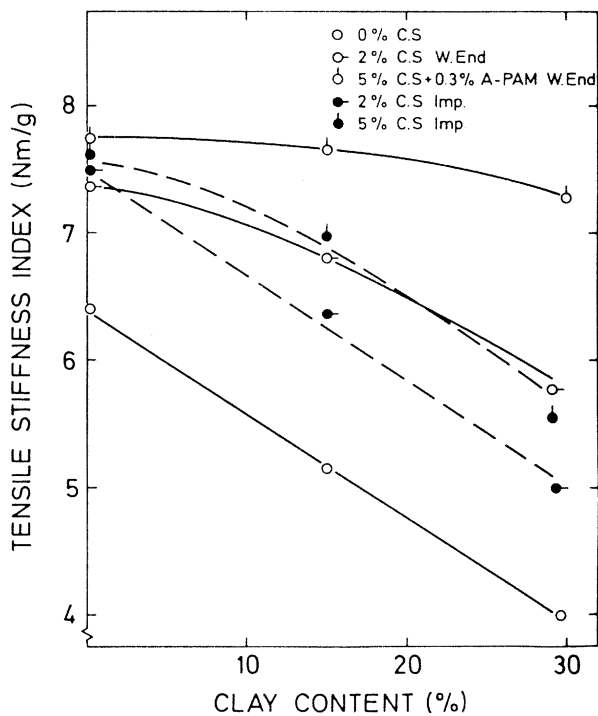
### **Comparison between Cationic Starch Wet-End Addition and Web Impregnation**

In order to gain some insight into the mechanism of action of starch, wet-end addition was compared with an impregnation procedure where the dried sheets were dipped in a solution of CS, couched and dried again under biaxial restraint. The results are given in Figs. 4-7 and in Table 3. For unfilled sheets the strength improvements obtained by wet-end addition are similar to those obtained by the impregnation procedure, whereas wet-end addition is superior to the impregnation procedure for paper sheets having a higher filler content. On the other hand, wet-end

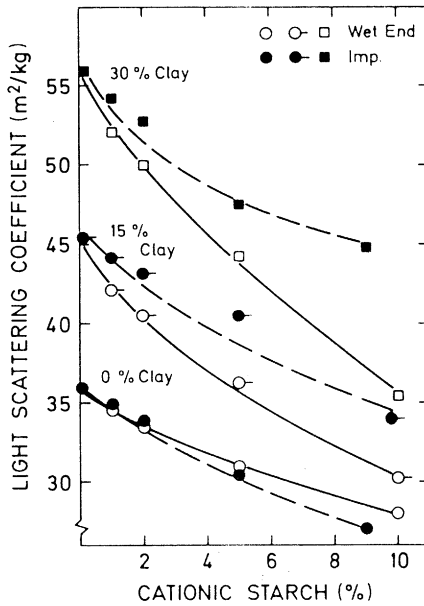
addition causes a greater decrease in light scattering coefficient than impregnation, as shown in Fig. 6. The difference is similarly more accentuated for filled sheets.



**Fig 4**—The effect of cationic starch addition on the tensile index of clay-filled papers. Comparison between wet-end addition (W. end) and impregnation addition (Imp.)



**Fig 5**—The effect of cationic starch on the tensile stiffness index of clay-filled papers. Comparison between wet-end addition (W. end) and impregnation addition (Imp.)

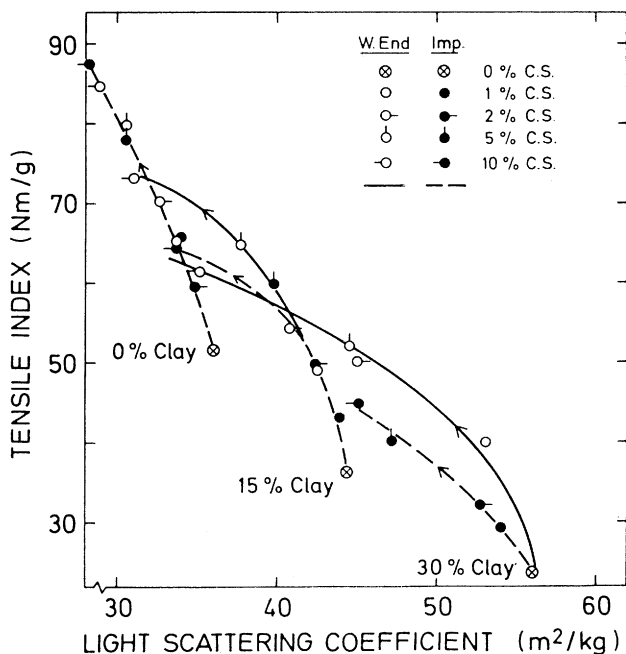


**Fig 6**—The effect of cationic starch on the light scattering coefficient of clay-filled papers. Comparison between wet-end addition (W. end) and impregnation addition (Imp.)

Clay content	Starch addition	Tensile index	Tensile stiffn index	Strain to failure	Light scatt coeff	Density
%	%	kNm/kg	MNm/kg	%	m <sup>2</sup> /kg	kg/m <sup>3</sup>
30	-	23	4.0	1.2	56	560
30	5% (imp)	36	5.5	1.6	47	580
30	4.2% (w-end)	52	7.2	2.1	45	642

**Table 3.** Properties of filled paper sheets - comparison between wet-end addition (w-end) and impregnation (imp) addition of cationic starch.

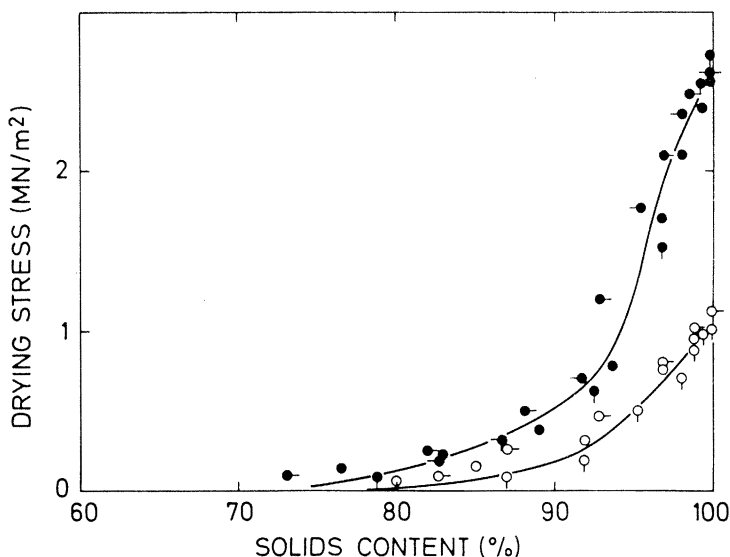
It is shown in Table 3 that the apparent sheet density is increased to a much larger extent by wet-end than by impregnation addition. Fig. 7 shows the relationship between tensile index and light scattering coefficient for the two cases when CS is added at the wet end and by an impregnation procedure. For unfilled sheets the tensile index versus light scattering curve coincides for the two addition modes, whereas a wet-end addition is preferable to impregnation addition of CS in the case of filled papers.



**Fig 7**—The effect of cationic starch on the relationship between the tensile index and the light scattering coefficient for clay-filled papers. Comparison between wet-end addition (W. end) and impregnation addition (Imp. )

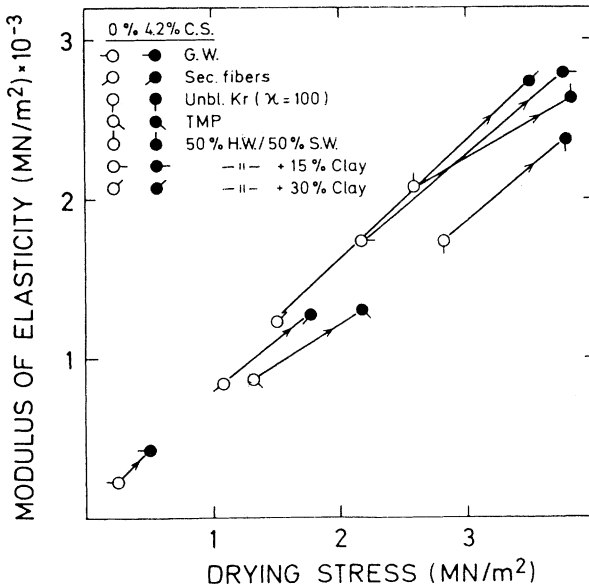
## Drying Stresses

Our data clearly indicate that the wet-end addition of CS improves sheet consolidation and that the tensile stiffness index  $E/\rho$  (or modulus of elasticity) is strongly improved only for papers having a high filler load. In view of the known fact (8, 9) that the modulus of elasticity is closely correlated to the drying stress set up during drying under restraint, and that the drying stress level reflects sheet consolidation, the effect of CS wet-end addition on the building up of drying stress during the drying of various paper sheets was studied.



**Fig 8**—Drying stress versus solids content for sheets containing 50% clay. Unfilled symbols = no starch added; filled symbols = 4.2% cationic starch and 0.3% anionic polyacrylamide added. Bleached softwood kraft pulp, 20°SR

Typical results are illustrated in Fig 8 for the drying stress versus solids content for a sheet containing 50% clay and a sheet containing 50% clay with 4.2% CS and 0.3% A-PAM. In this particular case the total drying stress increased from 1.1 MN/m<sup>2</sup> to 2.6 MN/m<sup>2</sup> when CS was added. Results from a number of similar experiments using different paper furnishes have been collected in Fig. 9. Several conclusions can be drawn. Firstly, all data are gathered close to a straight line corresponding to: drying stress = 10<sup>-3</sup> x modulus of elasticity.



**Fig 9**—The effect of cationic starch on modulus of elasticity and drying stress for different papers made from different stocks. GW = Groundwood pulp, 100 CSF; Sec. Fibres = Secondary Fibres; Unbl Kr. = Unbleached softwood kraft pulp, kappa 100; TMP = thermomechanical pulp; HW = Bleached hardwood kraft pulp, 25°SR; SW = Bleached softwood kraft pulp, 25°SR

This same relationship was previously obtained by Htun (8, 9) for paper webs without any wet-end additives or clay fillers. Secondly, the relative increase in drying stress and modulus upon addition of CS is more accentuated the higher the filler load. As shown in the figure, it is not the low strength level per se which determines the improvement obtained by starch addition. The absolute increase in drying stress and modulus is generally lower for pulp furnishes without filler irrespective of the strength level without CS.

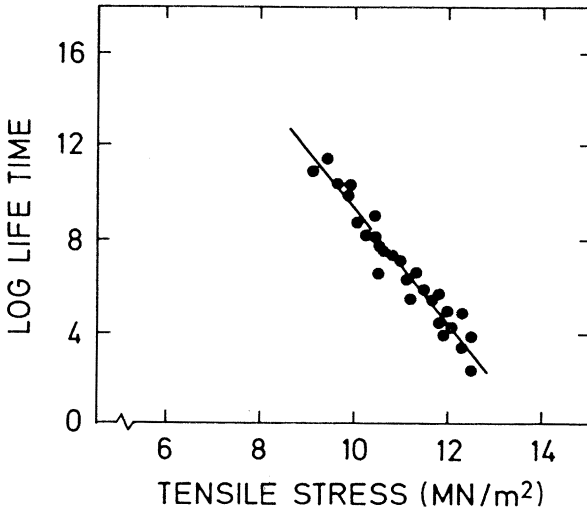
### **Stress Concentrations**

During the course of this work, various approaches were investigated in order to evolve new information regarding the mechanism of the action of hydrophilic mucilages such as CS on filled papers. One approach was to determine the level of stress concentrations in paper sheets. This was done by measuring the time to failure under tensile load (lifetime) of paper sheets made for bleached softwood kraft pulp with different clay loadings up to 40% and various additions of cationic starch. Figure 10 shows typical lifetime data versus applied tensile stress. The results of these measurements are given in Table 4, showing both the stress concentration factor  $j$ , and the activation energy for tensile failure. The measurements were performed in the cross direction (CD) for sheets containing 0 and 20% clay and in both the machine direction (MD) and the CD for sheets containing 40% clay.



Clay content %	Starch addition %	Stress concentration factor $\frac{\text{kJ}\cdot\text{kg}}{\text{mol}\cdot\text{Mn}\cdot\text{m}}$	Activation energy kJ/mol
CD-strips:			
-	-	254 ( $\pm 42$ )	157 ( $\pm 11$ )
-	0.5	176 ( $\pm 26$ )	140 ( $\pm 8$ )
-	2	206 ( $\pm 23$ )	158 ( $\pm 7$ )
-	5	174 ( $\pm 13$ )	163 ( $\pm 6$ )
20	-	482 ( $\pm 88$ )	164 ( $\pm 14$ )
20	0.5	640 ( $\pm 116$ )	227 ( $\pm 24$ )
20	2	287 ( $\pm 28$ )	163 ( $\pm 7$ )
20	5	234 ( $\pm 28$ )	160 ( $\pm 8$ )
40	-	2510 ( $\pm 810$ )	252 ( $\pm 52$ )
40	0.5	1320 ( $\pm 191$ )	243 ( $\pm 22$ )
40	2	1060 ( $\pm 260$ )	226 ( $\pm 33$ )
40	5	296 ( $\pm 40$ )	151 ( $\pm 9$ )
MD-strips:			
40	-	533 ( $\pm 150$ )	298 ( $\pm 57$ )
40	0.5	266 ( $\pm 75$ )	191 ( $\pm 29$ )
40	2	129 ( $\pm 43$ )	156 ( $\pm 22$ )
40	5	100 ( $\pm 19$ )	165 ( $\pm 15$ )

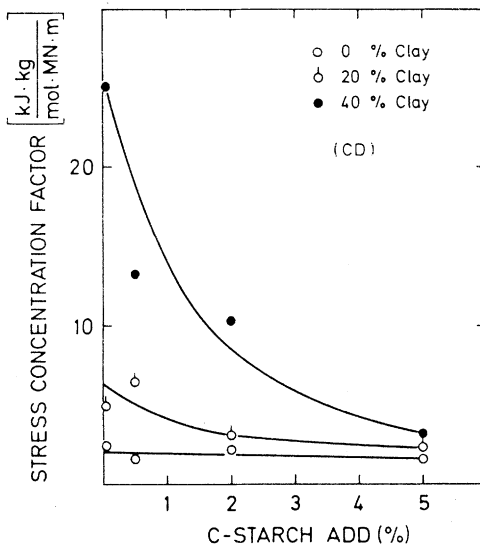
Table 4. The stress concentration factor and the activation energy for tensile failure of paper sheets (bleached softwood kraft, 23 SR) at various clay loadings and starch additions.



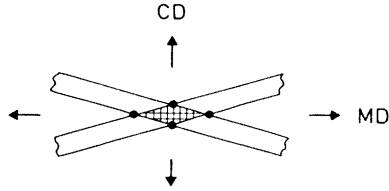
**Fig 10**—A typical plot of lifetime versus tensile stress for a filled paper where starch has been added at the wet-end

In Fig. 11 the  $j$  factor in the CS has been plotted versus the CS addition in papers containing 0, 20 and 40% clay. It is obvious from Table 4 and Fig. 11 that the intensity of stress concentration in sheets having a high filler loading is significantly decreased by the CS wet-end addition. It is also clear that an increased filler loading increases the stress concentration factor. In general, the stress concentration factor is much higher in

the CD than in the MD. This is also to be expected from simple physical considerations of the stress distribution around a fibre crossing, when an assembly of fibres is stressed in the CD compared with stressing in the MD (see Fig. 12).



**Fig 11**—The stress concentration factor,  $j$  (CD) versus cationic starch addition at various clay filler loadings. Bleached softwood kraft pulp, 25°SR



Local stress concentrations  
in a fibre crossing

The activation energy for most of the paper sheets is about 150-200 kJ/mole. Although it appears that the activation energy is slightly increased by a high filler loading and decreased by the CS addition at high filler levels, the effects are not considered to be of magnitude to require any closer interpretation.

## DISCUSSION

Based on the experimental data presented in this paper a hypothesis for understanding the effects of wet-end addition of hydrophilic mucilages on the properties of filled papers has evolved. Several important observations have been taken into account.

Firstly, it has been shown that the strength improvement obtained by cationic starch wet-end addition is more dramatic with filled papers than with unfilled papers.

Secondly, there is little difference between wet-end addition and impregnation addition to unfilled papers, whereas wet-end addition is superior to impregnation

addition on filled paper sheets. This fact, together with the fact that the sheet density is greatly increased in the case of wet-end starch addition to filled paper, indicates that wet-end addition improves the sheet consolidation procedure for filled papers.

Thirdly, wet-end starch addition greatly increases the drying stress set up during drying under restraint. Again the effect of starch addition is more accentuated the higher the filler level.

Finally, it has been shown that the level of stress concentration can be greatly decreased by a wet-end addition of starch to a filled paper sheet, whereas the effect on unfilled paper sheets is much smaller.

It should be noted that these observations are probably not restricted to cationic starch additions. Unpublished data show that the effects are by no means related to the specific nature of the starch (i.e. charge density etc). It appears rather as though the observations made are general for the additives which we may classify as hydrophilic mucilages. Chemical modifications are mainly tools for getting the additives adsorbed onto the papermaking raw materials. The main object of our hypothesis is to explain how a hydrophilic mucilage may act to decrease the level of stress concentrations in highly filled papers.

A schematic illustration of this "stick-slip" hypothesis is given in Fig. 13. To the left in Fig. 13 a local event between two fibre surfaces during consolidation (drying) is pictured. During drying a certain local drying stress ( $\sigma_t, \sigma'_t$ ) is created in the sheet structure. A filler particle acts as a dislocation between two fibre surfaces and is subjected to a certain shear stress mediated through the fibre surfaces. If the local friction between the filler particle and the fibre surface is large ("stick"), the drying stress may eventually exceed the local failure stress. If local failure occurs, the water meniscus is broken up, the reconsolidation of this bond during the subsequent drying is not likely to occur. This local failure will of course lead to an increase in the light



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## Transcription of Discussion

### The Dry Strengthening Effect of Cationic Starch Wet End Addition of Filled Papers

by T. Lindström, P. Kolseth and P. Naslund

**Caulfield** I would like to point out that Zhurkov's equation was derived in 1954-56 by Bernard Coleman, published in Journal of Polymer Science. The derivation is based on Eyring's theory of reaction rate kinetics with the simple creep rupture hypothesis of St. Venant.

**Dr. T. Lindström** The Zhurkov equation is semi empirical with no scientific basis. I would like to have that reference later. The Eyring theory is considered to be semiempirical.

**Dr. B.A. Nazir** Wiggins Teape R & D, Beaconsfield, England

What is the difference between tensile index and tensile stiffness? What is the physical significance of these two terms? Should we expect a difference between these two when we add filler? Your Figures 4 and 5 show a great difference.

**Lindström** If we have good bonding in a sheet, we may have a high modulus due to the fact that the filler particles are stiff. On the other hand, we are decreasing the amount of load-bearing cellulose and this is the reason why the tensile index cannot be improved to the same extent as the tensile stiffness. The best tensile we can get with starch is, presumably, the law of mixtures between cellulose and filler (the law does not apply without dry strength additives).

**Nazir** How do you measure the tensile stiffness index?

**Lindström** The tensile stiffness index is defined as the modulus divided by the density of the sheet. It is the slope of the stress strain curve taken from Instron measurements.



**Nazir** Referring to Figure 4 concerning the difference between wet end addition and impregnation, looking at 5% impregnated starch, tensile index reduces from 80 to 40 on addition of filler. Looking at zero addition of starch, one starts at 50 and drops down to 30. The strength loss with filler is very much greater when you have got starch in there. What is the explanation for that?

**Lindström** In a filled sheet, it is important to release these stress concentrations and in an unfilled sheet, with less stress concentrations, you can increase the bonding. If you have a sheet with filler, there is not sufficient affinity of the cationic starch which can aid the bonding between the fibres and the filler. If you have an unfilled sheet, with more cellulosic surfaces, the starch is presumably more compatible with them than with a filler surface. This may be the explanation.

**Nazir** Looking at this figure, one could conclude that addition of sizepress starch is inferior to wet end addition.

**Lindström** It is inferior in terms of strength properties. However, if you consider that you are adding it for surface as well as strength properties, then that is a different matter, e.g. for sheet impregnation process where you have a uniform distribution across the sheet. This cannot be compared with sizepress. In this laboratory experiment, the handsheet was dipped into a starch solution and this is not the same thing.

**Dr. R.C. Howard** UMIST, Manchester, England

If I understand what you are saying, the primary mechanism is not one of the starch sticking the fibres together. Am I right in my interpretation?

**Lindström** We cannot refute the glue hypothesis. We are trying to look at the problem from another angle. This is another type of hypothesis which we could use to increase our understanding of the process in the future. I cannot make an assessment of the relative importance of the two hypotheses.

**Prof J. Marton** Westvaco, Laurel, U.S.A.

Do you add the starch to the filler, fibre or to the furnish?

**Lindström** No, we add it to the whole slurry when the fibres and filler are mixed and then form the sheet. The starch is added as 5% on total (8% on filler).

**Marton** Do you reach the saturation point on the Langmuir starch adsorption isotherm of the system?

**Lindström** On the adsorption isotherm at 2% starch, you have full adsorption, whereas at 5% starch, you will only adsorb about 3.5% with this. By adding the anionic polymer, you are precipitating the excess amount of cationic starch onto the fibres, so the amount of the starch is quantitative which means you can still form a sheet with, for instance, 10% starch.

**Marton** What is the zeta potential of the final system?

**Lindström** We did not measure it, but I would speculate that it would not be too far from zero point. We are calculating the addition of the cationic starch from the amount of anionic polymer present. So, the system should be balanced.

**Marton** Should one wish to duplicate the work, are there any other process steps not mentioned?

**Lindström** No, nothing is missing.

**Bown** In Figure 12, I am not sure that the relative dimensions of the filler and the fibre are in proportion. In fact, filler particles are 4 - 5 microns in diameter, whereas fibres are 1 or 2 mm long. I think this is important because you don't have to invoke a hydrophilic slipping mechanism. You could explain your results by a mechanism which would be a filler fibre filler bond, i.e. the starch is capable of holding the fibres together with the filler in the middle. Without the starch there, the filler remains in its normal position in the pulp network and you don't really need to propose these mechanisms. With the physical scale of what is happening, the sort of mechanism you propose is not plausible.

**Lindström** I need an explanation for the decrease in stress concentration factor.

**Bown** Looking at your data, I think the explanation is actually there because if the fibres bond without the filler having any effect, in other words they bond over them, then you are back to the situation where the filler is not really there. You are back to the stress concentration that you had in the first place.

**Lindström** As I said in the beginning, we are only offering a hypothesis. We have difficulties in explaining the effect of starch on sheet consolidation and on the wet strength.

**Prof P. Luner** ESPRI, Syracuse, U.S.A.

In your hypothesis, you suggest a preferred orientation of the platelets both with and without starch.

**Lindström** No, this is not so. It was just a way to illustrate the effect. The wet strain increases considerably during the addition of wet end starch. I don't see how you can explain this if you don't invoke the hypothesis.

**Luner** I was going to suggest that this preferred orientation could be verified experimentally.

**Lindström** Generally, we find that you can get the strength improvements with spherical particles like calcium carbonate, etc. There appears to be no difference between different kinds of filler though the effect is larger with smaller particle size fillers.

**Thorp** What happened to the formation of the samples as you went up in filler and additives?

**Lindström** There is no problem when you use the Formette Dynamique. You could have problems on a paper machine, but that is another story.

**Prof R.H. Atalla** IPC, U.S.A.

The paper has a lot of practical implications which you haven't mentioned. Would you like to comment?

**Lindström** We added the anionic polyacrylamide and cationic starch straight into the stock system to see what happens, as you would in fact. This gave us formation problems on our experimental paper machine which meant we had to adopt different strategies, but still using cationic starch. Adding large amounts of starch to produce a high filled sheet is a viable technology.

**Atalla** Could you possibly be giving the filler the surface characteristics of a fiber by the addition of starch, i.e. essentially transforming an inorganic material into something with a carbohydrate surface which bonds well to the fibres. Then, the stress concentration factor would stem from the fact that there is a more homogenous distribution of stresses.

**Lindström** Exactly.

**I.K. Kartovaara** FPPRI, Helsinki, Finland

Referring to Figure 8, it shows that about 50% of final level in the drying stress is developed after 95% solid content. When you dried the sheets, was this to zero moisture content?

**Lindström** Yes.

**Kartovaara** Would this mean that if the correlation between drying stress and tensile stiffness index holds, then if you go on to a real paper machine where you dry to only 95% solids, then would you lose 50% of your advantage.

**Lindström** We have not studied this so we don't know the answer.