

# ON THE NATURE OF JOINT STRENGTH IN PAPER – A REVIEW OF DRY AND WET STRENGTH RESINS USED IN PAPER MANUFACTURING

*Tom Lindström,<sup>1</sup> Lars Wågberg<sup>2</sup> and Tomas Larsson<sup>1</sup>*

<sup>1</sup>STFI-Packforsk AB, Box 5604, SE-114 86 Stockholm, Sweden

<sup>2</sup>Dept. of Fibre and Polymer Technology, Royal Institute of Technology  
(KTH), SE-100 44, Stockholm, Sweden

## INTRODUCTION

The properties of paper are largely dependent on the bonds between the fibres. This is, of course, primarily true of those strength properties that are directly related to the number of bonds in the paper. Other properties are also dependent on such bonds, properties such as the opacity of the paper, its smoothness, porosity, dimensional stability, pore size distribution, linting propensity, density, stiffness, formation, and compressibility to mention a few.

The normal way of affecting the number of bonds in a paper is through the choice of fibre material and through a correct beating of the pulp. It is true that properties of paper may be manipulated through the choice of beater type, its specific edge load etc to expand the property or process space in paper manufacture. There are still many limitations as to what can be achieved by beating and other process tools, so the practical paper-maker is continuously looking for ways to expand property and process space to be able to manufacture new products or boost paper machine productivity.

In this review the terms “bonding” and “joint strength” will be used

interchangeably. “Joint strength” includes both the adhesion zone (2D zone of bonding) and the cohesion zone (3D zone of bonding).

Despite massive efforts over the years, our understanding of the molecular mechanisms of bonding is still in its infancy. There is still the fundamental argument as to the relative contribution of hydrogen bonds, ionic bonds, dipolar interactions, induced polar interactions, long-range van der Waals forces, and covalent forces (for wet strength resins) in various situations. Taken to the extreme, it was once believed that lignin contributed little to bonding in lignin-rich pulps, because they were assumed to be poor hydrogen bonding agents. Not anymore, as it has been realised that strong bonding can be created between mechanically liberated pulp fibres. Though critical experiments still need to be formulated to examine such matters, this review will not focus on them.

It is acknowledged, that hydrogen bond theories have been formulated by Corte and Shashek (1955), Nissan and Sternstein (1964) and others, but it has not been possible to further expand our knowledge from the initial formulations.

This review will instead focus on the use of various dry and wet strength additives to improve bond strength. The authors have made efforts to relate the discussion to the historical and current context of dry and wet strength resins, and to discuss more recent developments in understanding adhesive and cohesive failure.

Hence, after some general considerations and introduction to the concepts of process and property space in paper manufacture, a brief discussion of current paper strength theories will be made. A more detailed account of adhesive and cohesive failure mechanisms will follow, after which dry and wet strength resins will be reviewed. As far as wet strength agents are concerned, traditional wet strengthening will be given less emphasis; the focus of this later part will instead be on potential chemistries to alleviate tensile creep and compression creep under moist conditions.

## **DRY STRENGTHENING OF PAPER – GENERAL CONSIDERATION**

### **Literature overview – A historical context**

Early literature in the dry strength resin field was reviewed by Swanson (1950, 1956). The immense activity in this field after World War II is reflected by the fact that Swanson lists no fewer than 215 papers published between 1946 and 1956. The early literature is very much focused on polysaccharides, such as gums and cellulosic derivatives. Updated reviews were also published by Swanson (1960, 1961). The role of polysaccharides in inter-fibre bonding was

accounted for in more detail by Cushing and Schuman (1959). These reviews provide a good account of many generic observations. At that earlier time, dry strengthening agents were referred to as “beater additives”, and the application of such additives was based on their natural affinities for wood fibres. The subsequent development of cationic starches in following years made many of the gums extensively studied during this earlier period almost obsolete. Around 1980, a number of excellent reviews were published [Davison 1980; Hofreiter 1981; Reynolds 1980; Reynolds Robinson 1980 and Wasser 1980]. These reviews provide the modern view of the action of dry strength resins.

There are also more recent textbook chapters on the subject, but they are mostly at the introductory level [Eklund and Lindström 1991; Ketola and Andersson 1999; Marton 1991].

The most recent review in the field [Pelton 2004] provides the reader with some interesting contemporary views on the subject.

### **Dry strength of paper – General consideration**

Adopting a simple approach to paper strength, strength is seen to depend on at least the following factors:

- Fibre strength and length
- Fibre bond strength, i.e. specific bond strength (SBS) and relative bonded area (RBA)
- Sheet formation
- Stress distribution-residual stresses

The magnitude of the dry strengthening effect of commercial additives is generally smaller than the effects of pulp beating on paper strength. Therefore, it is easily realized that when dry strength resins are being evaluated, care must be taken to determine to what extent variables such as sheet formation, fines retention, and wet pressing can be controlled, particularly in the light of the effects to be considered.

Sheet formation has a strong and well-known effect on strength [see e.g. Hallgren and Lindström 1989; Horn and Linhart 1991; Norman 1965], and many dry strength resins are cationic and affect both retention improvement and the associated deteriorated formation. Thus it is very difficult to compare the effects of dry strengthening agents based on experiments performed in different laboratories under different sheet-forming conditions.

In a classic study published in 1954, Leech tried to resolve some of these issues. Leech found that the increase in strength brought about by the

addition of locust bean gum is ascribed to increased strength of the bonds (60%), improved formation (25%), and an increased number of bonds (15%).

Fibre bond strength is presumably the most interesting aspect of dry strength resins. It is also quite clear that the fibre–fibre bond strength is the weak link in paper dry strength [Davison 1972; Page 1969], and the effects of dry strength agents are thus in most cases more pronounced in weak paper sheets. Stratton and Colson (1993) found that weak bonds fail at the fibre–fibre interface with little or no damage to the fibre surface. Stronger bonds tend to produce “picking” of microfibrils from the surface of one or both fibres. The strongest bonds produce failure at the S1–S2 interface of one or both fibres, with substantial tearing of the S1 layer. Hence, bond failure may be either adhesive or cohesive depending on the specific bond strength. General aspects of fibre–fibre bonding have also been reviewed by Uesaka et al (2002).

Adopting the classic approach, the relative bonded area can be estimated from either the scattering coefficient of the sheet or, perhaps better yet, through the BET surface area of dry paper [e.g. Haselton 1955; Ingmansson and Thode 1959; Swanson and Steber 1959].

In light of modern concepts of the fibre cell wall as a swollen gel, it is not self evident to what extent added dry strength adjuvants either act internally in the cell wall of fibres or aid adhesion in the surface layers of fibres. It was, for instance, suggested many years ago by Spiegelberg (1966) that the effect of hemicellulose on fibre strength is to allow more efficient redistribution of stress to occur when the fibre is subjected to an external load. It was more specifically suggested that hemicellulose in the cell wall acted as a protective colloid to prevent microfibril aggregation (through hydrogen bonding/co-crystallisation).

Though the effect cannot be ruled out, the collective weight of the evidence concerning the effect of polymer molecular weight on strength improvement suggests a surface adhesion mechanism. This is because it has been found by many authors that higher *M<sub>w</sub>* adjuvants enhance strength better than low *M<sub>w</sub>* adjuvants do [Allan and Reif 1975b; Brouwer 1997; Pelton et al 2004; Thompson et al 1953; Zhang et al 2001]. It has also been found that low charge density polymers, for example, low charge density polyacrylamide (PAM), protruding out in solution is a more effective dry strengthening agent than high charge density PAM is [Park and Tanaka 1998].

There are basically two reasons why dry strength adjuvants are widely used by papermakers: they expand either paper property space or paper processing space.

As was stated many years ago by the late Alfred Nissan, “The task of the paper maker is to deviate from the relationships”. Typical mechanical

processes for expanding property space include TAD (Through Air Drying), drying for tissue paper, Condebelt drying for linerboard, and Clupac devices and Flakt drying for sack paper.

It has been observed and suggested that certain dry strength resins, such as starches, enhance both specific bond strength and the bonded area, whereas polyacrylamides [Yamachi and Hatanaka 2002] and CMC grafting (see below) primarily tend to improve the specific bond strength. The difference is that those bonding agents that improve the specific bond strength but not the relative bonded area tend to maintain bulk, whereas those that enhance the relative bonded area tend to increase sheet density. As beating increases sheet density, it is often beneficial to use an agent that primarily improves the specific bond strength, if, for example, opacity or bulk is a desirable property. In other cases, for example, in the manufacture of liner materials, agents which increase sheet consolidation can be greatly advantageous.

Dry strength treatments are not expected to affect the flexibility of fibres; rather, a dry strength agent is expected to affect bond strength and/or sheet consolidation. Many dry strength agents may be classified as gelatinous mucilages, from which it is hypothesized that they may stabilize the water meniscus during drying, by delaying the breakage of the meniscus until a higher dry content is achieved. This concept goes back to the classic consolidation experiments of Lyne and Gallay (1954). Hypothetically, a dry strength agent could be a pure consolidation agent, and hence the dry strengthening effect should be similar to that of wet pressing. If, on the other hand, the dry strengthening mechanism works only by improving the specific bond strength, there is an opportunity to expand paper property space.

It has also been shown that certain adjuvants may decrease the build-up of stress concentrations during drying [Lindström et al 1985]. Hence, there are now at least three separate mechanisms by which dry strength agents may work:

- By consolidating the sheet – i.e. by affecting the Campbell forces
- By increasing the specific bond strength
- By decreasing the local stress concentrations in the sheet

A hypothetical matrix as to the kind of influence such agents may have on sheet properties is given in Table 1. It must be emphasized, however, that most known dry strengthening agents work according to a mixture of different mechanisms and not a single one.

The ultimate challenge is to develop dry strength agents that can replace beating. This would have fundamental impacts on sheet quality, such as decreased CD shrinkage on paper machines (due to a decreased swelling of

**Table 1** Hypothetical matrix relating different strengthening agents with paper properties as treated in the literature

Type of strengthening agent	Tensile strength	Modulus of elasticity	Strain at break	Sheet density
Consolidation agents	+	+	+/-	+
Bond strength agents	++	0	+	0
Stress release agents	+	+	++	0

fibres), resulting in improved sheet edges, surface smoothness, and dimensional stability.

Probably one of the most important aspects of dry strength agents is their ability to expand paper processing space. Beating fibres increases the swelling of fibres, which is a fundamental restriction in wet pressing. By replacing beating with the use of dry strengthening agents, the solids content after wet pressing can be enhanced and, on dryer-limited paper machines, productivity can be boosted. This effect has been known for many years [Reynolds 1980], but has seldom been conveyed to the practical papermaker.

### **Paper strength and the load elongation curve**

The structure of the inter-fibre joints and the physical and chemical nature of the forces responsible for them are still areas of significant debate. The inter-fibre joints in paper are responsible for the mechanical properties of paper. The large number of fibres typically found in a fibre network, such as a paper, and the complex geometrical distributions of the individual fibres present in a paper are properties that make the theoretical description of paper difficult. This difficulty is compounded by the fact that the theoretical description of the interactions between fibres (inter-fibre joints) involves interplay between several structural dimensions. Van den Akker (1959) described the architecture of the inter-fibre joint as encompassing fibre-to-fibre, fibre-to-fibril, and fibril-to-fibril contacts. Ultimately, the inter-fibre joints are held together by inter-molecular forces, but, the geometric details of the inter-fibre joint may allow for the simultaneous action of several kinds of inter-molecular forces. It is also possible that the combination of all molecular forces may be synergistic [Van den Akker 1959].

Fibres and their potential for forming inter-fibre joints are affected by their origin and past history, such as wood species, cooking and bleaching conditions, and mechanical treatments (e.g. beating). From the perspective of

inter-fibre joint strength, the term “fibre” may represent a class of entities of various chemical and physical properties. Despite these complications, attempts have been made to formulate theoretical models for use in predicting the in-plane tensile strength of paper.

The aim has been to predict, for example, the in-plane tensile properties of paper (e.g. tensile index and elastic modulus) based on a set of properties characterising the constituent fibres and their interactions [Page 1969; Kallmes et al 1977a–d; Seth and Page 1983; Williams 1983; Carlsson and Lindström 2005].

The in-plane load–elongation curves or stress–strain curves of paper are recorded to determine tensile index, elastic modulus, strain at break, and tensile energy absorption. In principle, information regarding the state of inter-fibre bonding could be obtained from such measurements (Hansen 1993). Once a stress–strain curve has been recorded, it could be interpreted with the aid of a suitable theoretical model. One fundamental problem arises from what is known of the typical paper sheet. The test pieces used in measuring the tensile in-plane properties of paper are much longer than the typical constituent fibres. This means that the recorded signal comprises the contributions of free fibre segments, fibre segments participating in inter-fibre joints, and inter-fibre joints as such. To gain some understanding of the structure and nature of the inter-fibre joint, the composed signal must somehow be broken down into the separate contributions of fibres and inter-fibre joints. The most developed models are those of Page and Seth [Page 1969; Seth and Page 1983]. Two equations exist, one for the elastic modulus of sheets (Equation (1)) and one for the tensile strength of sheets (Equation (2)). Both equations were developed for sheets with random fibre orientation.

$$E_p = \frac{1}{3} E_f \left[ 1 - \frac{w}{L \cdot RBA} \sqrt{\frac{E_f}{2G_f}} \tanh \left( \frac{L \cdot RBA}{w} \sqrt{\frac{2G_f}{E_f}} \right) \right] \quad (1)$$

In Equation (1),  $E_p$  is the elastic modulus of paper,  $E_f$  is the elastic modulus of the component fibres,  $w$  is the mean fibre width,  $L$  is the arithmetic mean fibre length,  $RBA$  is the relative bonded area of the sheet, and  $G_f$  is the shear modulus of the component fibres for shear in the  $(L, w)$  plane (Seth and Page 1983).

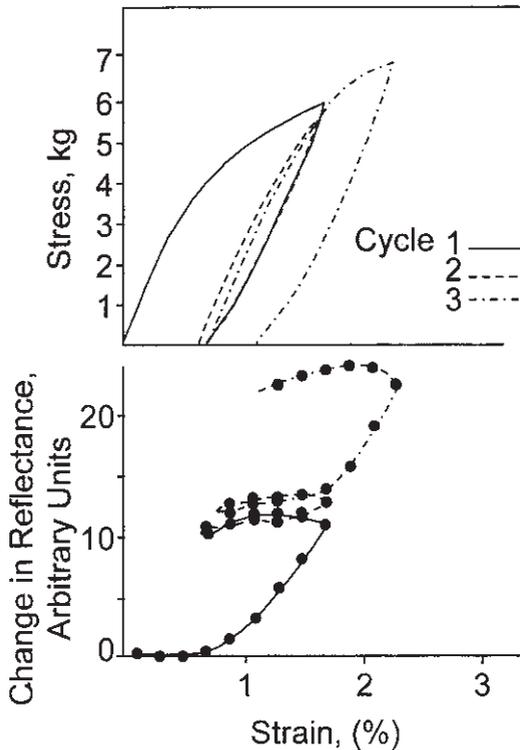
$$\frac{1}{T} = \frac{9}{8Z} + \frac{12A\rho g}{bPL(RBA)} \quad (2)$$

In Equation (2),  $T$  is the tensile strength expressed as breaking length,  $Z$  is the

finite-span tensile strength of the strip expressed as breaking length if no bond breakage had occurred (a derived quantity),  $A$  is the average fibre cross section,  $\rho$  is the density of the fibrous material,  $g$  is the acceleration due to gravity,  $b$  is the shear bond strength per unit bonded area,  $P$  is the perimeter of the fibre cross section,  $L$  is the fibre length, and  $RBA$  the relative bonded area of the sheet [Page 1969].

The relative bonded area (RBA) plays a central role in both these formulations. The strength of the inter-fibre joint, or the energy needed to completely separate the joined fibres, is given by the product of the specific bond strength and the RBA. In both Equations (1) and (2) the RBA is estimated as:

$$RBA = \frac{(S_0 - S)}{S_0} \tag{3}$$

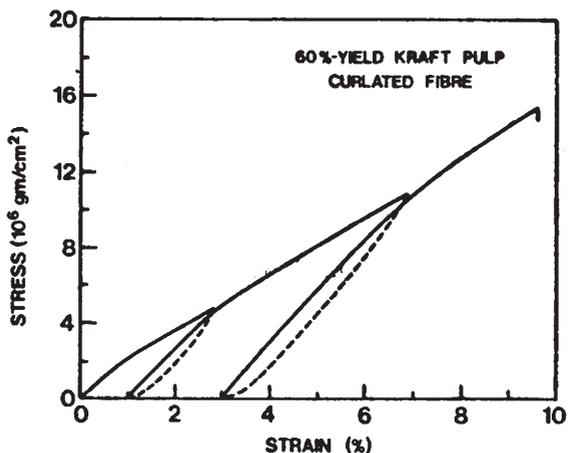


**Figure 1** Comparison between stress–strain curve and the corresponding curve, showing the change in reflectance. The figure shows Nordman’s data [Nordman 1958] and is taken from Page [Figure 1 on page 39 in Page 2002].

In Equation (3),  $S_0$  is the optical scattering coefficient of fibres in the unbound state and  $S$  is the optical scattering coefficient of the sheet. The reasoning underlying Equation (3) is articulated in a paper by Nordman (1958). Nordman presented experimental data that showed a strong correlation between changes in reflectance (related to the scattering coefficient via the Kubelka–Munk theory, see Borch 2002) and stress, recorded for paper during the cyclic loading and unloading of the test pieces (Figure 1). Based on this observation and the fact that the light scattering coefficient remained essentially unchanged during the elastic loading of the paper test pieces, Nordman concluded that the onset of plastic behaviour in the load–elongation curve recorded for paper coincided with the starting point of inter-fibre bond rupture.

Based on his conclusions, Nordman combined the estimates of changes in surface area with measurements of the irrecoverable energy loss during a loading/unloading cycle, and was able to calculate estimates of specific inter-fibre bond strength. This suggested a very appealing approach for interpreting the load–elongation curve recorded on paper: behaviour in the elastic region was due to the fibre properties while behaviour in the plastic region was determined by the properties of the inter-fibre joints.

However, the findings of Nordman have been disputed by Page; in fact, Seth et al (1983) have provided examples (Figure 2) of curves recorded for



**Figure 2** Typical stress–strain curve for 60% yield kraft pulp fibres of black spruce in which microcompressions were introduced by high-consistency curling action.

Figure taken from Seth and Page [Figure 8 on page 430 in Seth and Page 1983].

individual fibres that show load–elongation behaviour similar to that typical of paper sheets [Seth and Page 1983].

Hence, no definite statement can be made regarding the processes occurring in the sheet during loading outside the elastic region. Furthermore, a recent article by Page (2002) questions the conclusions of Nordman and suggests an alternate interpretation of his data. According to Page (2002), the stress–strain curve recorded for paper is controlled by the elastic and plastic behaviour of the fibres, and the observed partial bond rupture is strain controlled and an incidental consequence of the deformation of the fibres.

Other criticism has been directed towards the work of Seth, Page, and Kallmes et al [Page 1969; Kallmes et al 1977a–d; Seth and Page 1983 and Williams 1983]. de Ruvo et al (1986) criticised the results of the shear-lag analysis [Anderson and Houbolt 1948; Cox 1952] in general, as well as the lack of predictive power of the theories of Page and Kallmes, a lack stemming from the limited amount of data available regarding the fundamental parameters (e.g. fibre strength, bond strength, and relative bonded area) of their theories.

Räisänen et al (1997) critically evaluated the validity of the shear-lag model according to Cox (1952), and compared results from the Cox model with computer simulations of random fibre networks (finite element method – FEM) and with a simple force-balance approximation. They concluded that the shear-lag model is not applicable to random fibre networks and that the dominant stress transfer mechanism in random fibre networks and short fibre composites is quite different from that of the shear-lag model.

A different approach to understanding the in-plane tensile properties of paper has been taken by researchers such as Heyden (2000). de Ruvo et al (1986) had already suggested that as an alternative to the “descriptive theories of paper”, finite element method analysis (FEM) calculations should be used. The network nature of paper has led to work in which FEM calculations have been combined with computer simulations of networks. The thesis of Heyden (2000) used a combination of computer simulations and FEM calculations and contained an extensive review of network modelling work. A combination of computer simulations for network generation and FEM calculations for analysis has been used to create models of both two- and three-dimensional networks of cellulose fibres. Several interesting results regarding two-dimensional networks were presented, such as the degree of network activation as a function of both density and fibre length. But as Heyden points out, there is still a lack of knowledge regarding the properties of the inter-fibre bond. Hence in making simulations and calculations, assumptions must be made regarding both the nature and the strength of inter-fibre bonding. Ultimately, it would be interesting to compare simulation results and

experimental data, but it is currently difficult to judge what could be inferred about the nature of the inter-fibre joint from such a comparison.

Attempting to draw conclusions about the structure of and interactions in the inter-fibre joint by performing in-plane tensile measurements is difficult if not impossible. In a review of the in-plane tensile properties of paper, Niskanen and Kärenlampi (1998) discuss factors that influence various aspects of the in-plane tensile strength of paper. During paper manufacturing the fibre material is subjected to numerous processing steps that affect the fibres' tendency to form inter-fibre joints. However, the influence of these processing steps on the microscopic parameters of, for example, the Page equation(s) is not straightforward. Beating may function via both fibre surface activation (increased RBA) and the reduction of fibre curl. To interpret load–elongation curves using any of the above-mentioned models, reproducible data is necessary. This is complicated by the fact that the shape of the load–elongation curve is strain-rate dependent. The load–elongation curve seems to display the influence of some dynamic process that affect virtually all the measurable parameters associated with the in-plane tensile strength of paper.

There are two major obstacles to using load–elongation curves as a tool for diagnosing the state of the inter-fibre joint: the measurement of RBA and rate dependence in the load–elongation curve. The nature and morphology of the fibre wall make these measurements difficult and little is known of the molecularly bound area in inter-fibre joints. Even if the experimental difficulties could be overcome, the rate dependence in the load–elongation curve still impedes the obtaining of representative and reproducible data. Given Heyden's results (2000) concerning the degree of network activation, it is not obvious that all the inter-fibre joints present in a paper sheet will be activated as load-bearing elements, even in the case of infinitely slow strain rates.

The conclusion must be that until sufficient detailed structural, physical, and chemical knowledge is accumulated about the inter-fibre joint and the statistical-structural aspects of the paper sheet, the relevance of these macroscopic theories cannot be fully evaluated. Obtaining detailed knowledge of the inter-fibre joint is still somewhat hampered by the lack of experimental methods for the direct measurement of relevant fibre properties and inter-fibre interactions, a situation already observed by Van den Akker (1959). Progress has recently been made in several measurement areas, such as atomic force microscopy (AFM), quartz crystal microbalance (QCM), and other wet chemical techniques, and results that shed light on these central areas of understanding are now emerging.

It is, however, appropriate to emphasise that from a qualitative perspective the theoretical descriptions advanced by Cox (1952), Kallmes et al (1977a–d),

Page (1969), Seth and Page (1983), Heyden (2000), and others have provided important insights into the impact of inter-fibre joint strength on paper sheet properties.

### **Wet web strength**

Little work has been conducted in the field of additives to improve the wet web strength of paper. The classical publication by Lyne and Gallay (1954) provided a first insight to the consolidation of paper suggesting the link between Campbell forces, wet web strength and additives using glass fibres as a model system. More recently, Laleg and Pikulik have studied the effects of additives on wet web strength and Page (1993) has provided a theoretical framework based on the fibre-fibre wet friction.

Laleg and Pikulik (1991b, 1992) found that chitosan was an efficient wet-web strengthening aid for mechanical pulps and suggested that the amino groups could form Schiff's bases and react with aldehyde groups onto cellulose. These authors also studied the role of cationic starch derivatives on wet web strength of paper. Whereas, regular cationic starch did not improve the wet web strength of paper [Laleg et al 1991a; Laleg and Pikulik 1993b] cationic aldehyde starches [Laleg and Pikulik 1991c, 1993b] did improve wet web strength. The mechanism was assumed to be hemiacetal formation between the aldehyde groups and cellulosic hydroxyl groups.

The various mechanisms suggested for wet web strength were, however, never confirmed in model experiments.

It is quite obvious that the missing link in understanding is the connection between friction and adhesion in wet fibrous networks. Modern equipment (e.g. AFM) for studying surface interactions may reveal the nature of such interactions and work is underway in several laboratories to do so [e.g. Paananen et al 2003].

## **THE FORMATION OF FIBRE-FIBRE JOINTS AND THE NATURE OF THE JOINED AREA**

### **General**

The type of chemical interactions active in fibre/fibre joints, and the influence these interactions have on joint and paper strength, have long been an area of controversy and debate. There is still no clear ranking of the relative importance of different types of interactions, such as van der Waals and polar interactions.

To optimise paper properties, there have been considerable efforts to

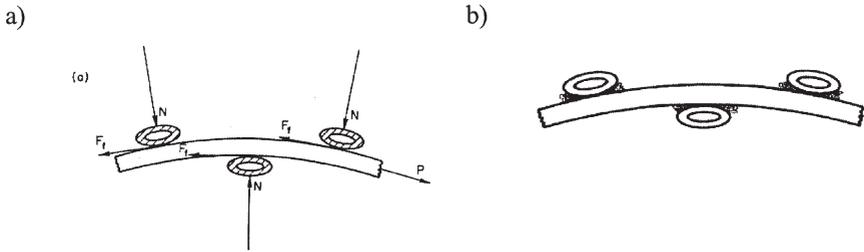
prepare paper with unique properties by modifying the interaction between the fibres via various experimental procedures. This is an almost overwhelming task, and considering the latest achievements in paper physics regarding the end-use properties of paper, this area has acquired yet another dimension of complexity. One of the purposes of the present paragraph is thus to summarise what is known of the interactions in fibre–fibre contacts, and how these can be modified to tailor paper properties by tailoring the joint properties.

Another purpose is to describe other important factors in the formation of strong fibre–fibre joints, from collision between fibres in the wet state, via consolidation of fibres during pressing and drying, to the relationship between joint strength and paper strength in the dry state.

### **Contact formation between the fibres**

The fibre–fibre contacts necessary for the development of the mechanical properties of dry paper are already formed, even as fibres are colliding in the forming section of the paper machine [Mason et al 1950; Mason et al 1958; Mason et al 1961; Kerekes 1986; Swerin and Ödberg 1997]. Mason (1950) determined early on that the frequency of fibre–fibre collisions could be related to the volume concentration of the fibres, the length: diameter ( $l: d$ ) ratio of the fibres, and the shear conditions of the fibre dispersion. Kerekes (1986) also described in some detail how the interaction between fibres in the wet state would control their tendency to form efficient fibre–fibre contacts for the formation of fibre flocs. Without going into too much detail, Kerekes (1986) stressed that fibres should have at least three contacts each to form a floc, and that the normal forces between fibres, from elastic fibre bending, and the friction coefficient in the contact zones between the fibres are important factors controlling the fibre–fibre interaction and the strength of fibre flocs. Swerin and Ödberg (1997) also showed that the addition of wet-end chemicals would change the conditions for floc formation due to a change of the molecular contact in the fibre–fibre contact zone. A schematic representation of these two different situations is shown in Figure 3.

Figure 3a) depicts the mechanical forces arising from elastic fibre bending [Kerekes 1986], and Figure 3b) depicts the additional forces arising from chemical additives in the fibre–fibre contacts, shown as increased contact area in this figure [Swerin 1997]. Earlier discussions concerning the influence of the interactions in the fibre–fibre contact zones have entirely focused on the flocculation behaviour of the fibres, but no doubt these interactions are also important for the initial consolidation between fibres as the water is removed from the papermaking web. It was also shown [Swerin 1998], via rheological

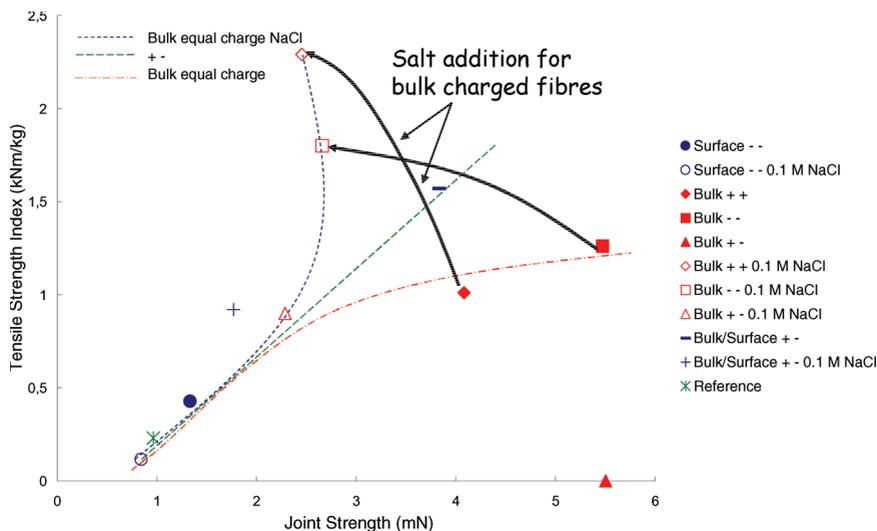


**Figure 3** Schematic representation of the mechanical forces, a), and chemical interactions, b), holding the fibres together in fibre networks at low fibre concentrations. In b) an increased concentration of the additives is indicated in the fibre–fibre crosses. Adapted from a) Kerekes et al (1986) and b) Swerin and Ödberg (1997).

investigations, that the critical fibre concentration for floc formation decreased significantly as polymeric flocculants were added. Since the structure of the fibre flocs is maintained in the paper, it might be suggested that if the fibres show great interaction in the wet state, i.e. the fibres are early “locked in place relative to each other”, the higher the normal forces acting between the fibres, the more efficient the contact between the fibres in the final paper.

There have been rather few investigations on model systems regarding the influence of interactions between fibres in the wet state on the mechanical properties of the final paper. However, it was recently demonstrated [Torgnysdotter and Wågberg 2004] that when the electrostatic interactions between carboxymethylated rayon fibres decreased significantly, the joint strength between the fibres decreased while the sheet strength increased. This was shown by determining both sheet strength and fibre–fibre joint strength for bulk- and surface-charged carboxymethylated rayon fibres at different salt concentrations.

The results of this investigation are shown in Figure 4, in which the minus sign (–) in the legend corresponds to negatively charged and the plus sign (+) corresponds to positively charged fibres, “bulk” stands for bulk-charged fibres, and “surface” relates to experiments where only the fibre surfaces were charged. Different trends are found for the bulk-charged fibres and the surface charged fibres and the following conclusions were drawn regarding these different types of fibres.



**Figure 4** Correlation between fibre–fibre joint strength and sheet strength for different combinations of anionic surface- and bulk-charged fibres and cationic bulk-charged fibres. In the figure legend abbreviations are:

Filled circle (Surface—): two fractions of anionic surface-charged fibres have been mixed,  
 Empty circle (Surface—0.1 M NaCl): two fractions of anionic surface-charged fibres have been mixed in the presence of electrolyte,

Filled diamond (Bulk++): two fractions of cationic bulk-charged fibres have been mixed,  
 Filled square (Bulk—): two fractions of anionic bulk-charged fibres have been mixed,  
 Filled triangle (Bulk+-): one fraction of cationic bulk-charged fibres have been mixed with one fraction of anionic bulk-charged fibres,

Empty diamond (Bulk++ 0.1 M NaCl): two fractions of cationic bulk-charged fibres have been mixed in the presence of electrolyte,

Empty square (Bulk—0.1 M NaCl): two fractions of anionic bulk-charged fibres have been mixed in the presence of electrolyte,

Empty triangle (Bulk+- 0.1 M NaCl): one fraction of cationic bulk-charged fibres has been mixed with one fraction of anionic bulk-charged fibres in the presence of electrolyte,

Hyphen (Bulk/Surface+-): one fraction of cationic bulk-charged fibres has been mixed with one fraction of anionic surface-charged fibres,

Plus (Bulk/Surface+- 0.1 M NaCl): one fraction of cationic bulk-charged fibres has been mixed with one fraction of anionic surface-charged fibres in the presence of electrolyte,

Cross (Reference): Reference pulp.

All results correspond to regenerated cellulose fibres. Adapted from Torgnysdotter and Wagberg (2004).

### *Bulk-charged fibres*

As shown in the figure, sheet strength increases for bulk-charged fibres when the salt concentration increases, whereas joint strength decreases.

The observed behaviour was explained by the consideration of two simultaneous phenomena. Firstly, the inter-fibre joint becomes weaker at high salt concentrations as the result of a decreased fibre surface swelling (less molecular interactions). Secondly the addition of salt screens the electrostatic repulsion between fibres, allowing for the development of an increased number of inter-fibre contact points. Hence, at none or low additions of electrolyte there will be few but strong inter-fibre joints, as the strong electrostatic repulsion prevents some fibre-crosses to fully develop into inter-fibre joints during sheet consolidation. When the electrostatic repulsion is screened (at higher salt concentrations) fibre-crosses can more fully develop into inter-fibre joints during sheet consolidation, forming more bonds albeit weaker bonds.

In this scenario the effect of electrostatic repulsion is hence two-fold – it both influences the surface swelling of bulk-charged fibres and the electrostatic repulsion between the fibres. The electrostatic repulsion between the fibres will hence affect the development of the fibre network geometry in the wet state and the net effect of salt addition is a delicate balance between the two phenomena, both of electrostatic origin.

This discussion was based on the assumption that the fibre flexibility was unaffected by salt addition and this assumption has also recently been shown to be correct [Torgnysdotter and Wågberg 2004; Forsström 2004].

### *Surface-charged fibres*

Surface-charged fibres are less flexible than the bulk-charged fibres, so the decreased colloidal interaction between fibres in the presence of electrolyte will not lead to a larger number of inter-fibre contact points. Therefore, the decrease in inter-fibre joint strength brought about as the result of increased electrolyte concentration is directly reflected in a decrease in the tensile strength of the sheet.

It was also found [Torgnysdotter 2004] that upon spraying of the sheets, prepared from bulk charged fibres and surface charged fibres, with a NaCl solution after sheet forming but before drying only resulted in a decrease in tensile properties of the sheets.

These results are naturally somewhat controversial since, it could be said that the macroscopic dimension of papermaking fibres would rule out the importance of colloidal interactions between the fibres. However, it has clearly been demonstrated that forces of colloidal origin can have a profound

effect on the macroscopic properties of, for example, charged polyacrylate gels [Osada et al 1999; Osada and Gong 2002; Osada et al 2003]; this phenomenon could serve as a model of water-swollen wood fibre surfaces and likely even for bulk-charged fibres, since this interpretation is consistent with the results presented in Figure 4. It was also found [Osada et al 1999] that the friction coefficient between macroscopic gels was determined by “hydrodynamic lubrication of the solvent layer between the two gel surfaces, which is formed due to the electrostatic repulsion of the two gel surfaces”. Since the swelling of the gel increases at a higher charge of the gel, at the same time as the electrostatic repulsion changes, there is an intricate balance between the solid material of the gels, in contact under a certain load, and the electrostatic repulsion between the surfaces. For a certain anionic gel type it was, however, found that there was an increase in the coefficient of friction between the surfaces of two orders of magnitude as the salt concentration increased from  $10^{-2}$  M NaCl to 1 M NaCl [Osada 1999]. This is also consistent with the results discussed in conjunction with Figure 4. It was also found that on sliding two oppositely charged gels against each other, such a high frictional force occurred that the gels were ruptured [Osada 1999]. Unfortunately, the properties of sheets made from oppositely charged fibres could not be tested due to excessive flocculation of the fibres.

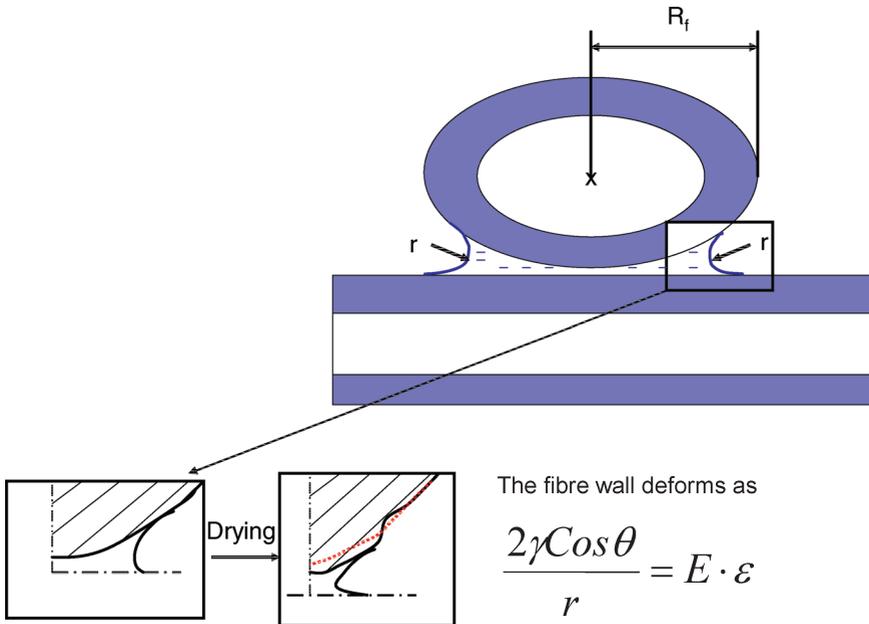
It should be stated, though, that this line of discussion is based on highly modified fibres but its application to actual wood fibre-based systems has been established. However, its general application naturally depends on the type of fibres used and their treatment. Nevertheless, the data presented in Figure 4 is an example showing that the connection between inter-fibre joint strength and sheet strength is, in the general case, not direct.

For clarity, it should finally be mentioned that the comparison between fibres and swollen hydrogels is relevant, since the external surface of wet fibres can be viewed as a swollen hydrogel [Pelton 1993]. In summary, this also means that the approach used for characterising the interaction between swollen and charged hydrogels can be very useful in characterising the interaction between charged fibre surfaces and the influence this might have on fibre–fibre joint formation and paper properties.

### **Development of the fibre–fibre joint**

When the distance between fibres in the wet state is short enough, the fibre–fibre interaction represents a balance between the capillary forces pulling the fibres together, the attractive van der Waals forces, and the repulsive electrostatic forces emanating from the negative charges on the fibres [Wågberg et al 1997]. The fibres are usually viewed as cylindrical shells interacting with each

other, but as mentioned earlier, the fibre surface is highly fibrillar [Clark 1985a], and these fibrils have a decisive influence of the development of the strength of the fibre–fibre joint [Clark 1985b]. New techniques for determining fibre structure via cryofixation and deep etching the fibres followed by field emission scanning electron microscopy (FE-SEM) have also recently been developed [Duchesne et al 2003]. These techniques have revealed a new, very open fibre wall structure in most commercial chemical pulps in their never-dried form, in which the fibrils are clearly separated. The openings between the fibrils are of the order of 10–50 nm, naturally depending on the degree of delignification, and the lateral dimension of fibril aggregates are shown to be of the order of 10–20 nm. This new knowledge, in combination with earlier well-established knowledge of the fibrillar structure of the fibre



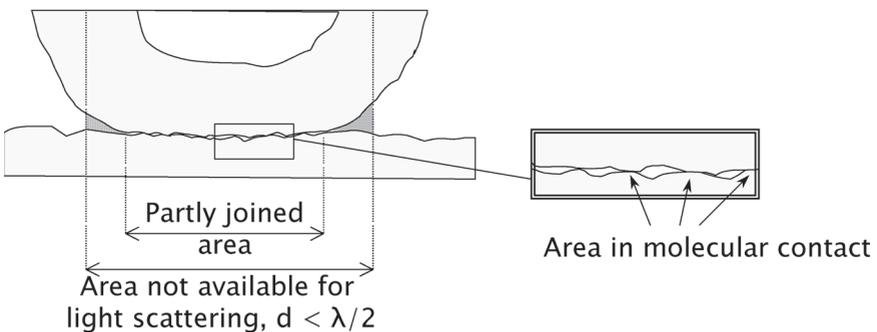
**Figure 5** Schematic representation of how the fibre wall deforms under the action of the capillary pressure in the water meniscus in the fibre–fibre contact. As the capillary radius,  $r$ , decreases, the pressure in the contact zone increases. This in turn increases the deformation of the fibre wall, which increases the area of contact between the fibres.  $R_f$  is the radius of the fibres,  $E$  is the transverse modulus of the wet fibre wall,  $\theta$  is the receding contact angle between the fibres and water,  $\gamma$  is the surface tension of the water, and  $\epsilon$  is the local strain of the fibre wall due to the capillary pressure.

surface, can naturally serve as a basis for new models of the interaction between fibre surfaces – models that remain to be developed.

When the fibres are brought into contact with each other under the action of the capillary forces between the fibres, the pressure in the water meniscus between the fibres deforms the fibre wall as schematically depicted in Figure 5.

Given that the wet transverse modulus of the fibre wall is low, i.e. in the order of 1 MPa [Scallan et al 1992; Nilsson et al 2001], the deformation (i.e. the local strain,  $\epsilon$ ) can easily reach approximately 1–10%. This will have a large influence on the contact area between the fibres, considering that water removal is a continuous process in which the capillary radius between the fibres continuously decreases as water is removed. Such processes have also been directly studied via microscopy of single fibre crosses, but at a higher solids content where the fibres are already in molecular contact [Page et al 1966].

Once the fibres are in contact, the details of the fibre–fibre contact can be described schematically as in Figure 6. There are several factors associated with this simplified view that need to be discussed before the details of the forces holding the fibres together are discussed. Light scattering measurements of sheets are usually used to detect the areas in molecular contact in a paper, i.e. the relative bond area (RBA) [Ingmansson et al 1959; Page 1969]. The assumptions underlying these measurements are based on earlier work [Haselton 1955] that established a correlation between light scattering and BET-specific surface areas arising from nitrogen adsorption. Since the wavelength of the light is much too large to enable detection of the dimensions of relevance for interactions between the fibres, it is difficult to justify light



**Figure 6** Description of the areas that might be detected using light scattering and the areas between the fibres in a fibre–fibre joint that are in actual contact. The inset also shows that there still might be areas in poor contact even in the partly joined area.

Picture courtesy of Mats Rundlöf, AB Capisco.

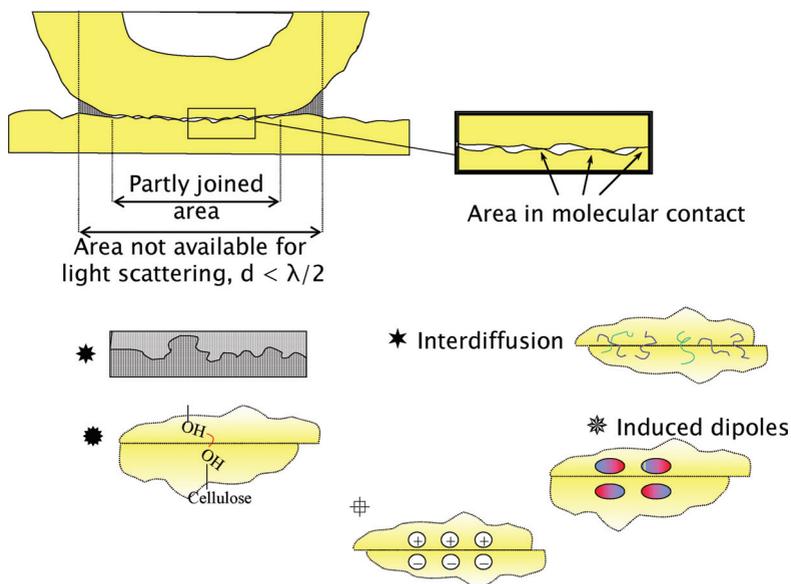
scattering measurements for the determination of RBA. This is indicated in Figure 6 as the shaded area outside the contact zone between the fibres. More recent work with the small-angle X-ray scattering of paper has also shown a linear relationship between BET areas and areas arising from X-ray scattering [Caulfield 1973]. However, the absolute values of the specific surface areas are vastly different, and therefore the correlations are valid for only one set of fibres and hard to transfer to others. Since different types of radiation, with significantly different wavelengths, were used in these experiments, it is maybe not so surprising that the results, in  $\text{m}^2/\text{g}$ , are different; after all, the structures that can be detected will be dependant on the wavelength of the radiation used. It is at present not known whether there is an ideal radiation wavelength for determining the “true” specific area of the fibre surface. However, the authors suggest that careful measurements with gas adsorption and BET analysis should be used to determine the specific surface area of fibres and papers.

From an engineering perspective it might still be reasonable to use light scattering measurements for paper product design purposes; however, such measurements cannot be used for determining fundamental properties of the joined area in a paper.

Inside the area of contact it is also necessary to distinguish between areas that are close enough to be affected by, for example, van der Waals forces, but not in direct molecular contact, and areas in direct molecular contact. This is important since some molecular mechanisms for enhancing adhesion between surfaces are dependant on a direct molecular contact between the surfaces [Johnson et al 1971].

After having defined these dimensions of importance, it might be useful to discuss the various mechanisms that can be cited in explaining the development and improvement of the adhesion between two surfaces. A schematic graphic representation of these mechanisms, following the general outline of Kinloch [Kinloch 1980, 1982], is shown in Figure 7.

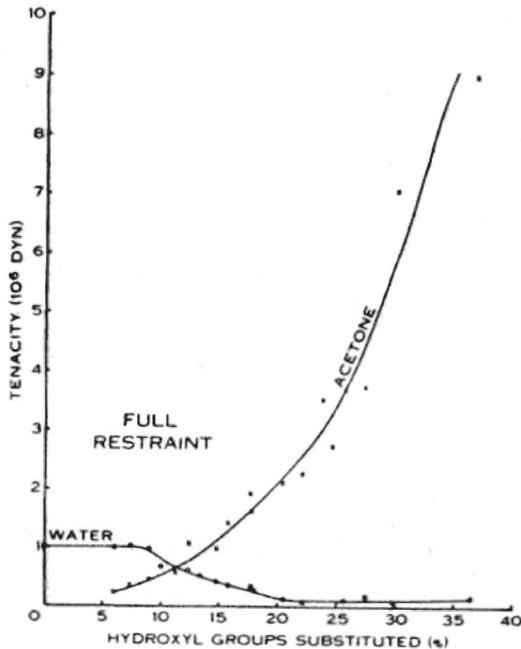
Since fibre surfaces are both rough and rather soft, they might adjust towards each other during the pressing and drying operations in the paper machine and therefore an *interlocking* mechanism whereby the fibre surfaces are locked in place relative to each other is thus likely to occur. This was indirectly proposed [Clark 1985a–b] as significant, since the fibrillation of the fibre surfaces seems to be so prominent. With a greater number of fibrils the strength of the fibre–fibre joint increases due to mechanical entanglement and/or an increased molecular contact area between the surfaces. For this mechanism to be operative there is no need for molecular contact between the surfaces, though molecular contact would of course add to the entanglement effect but as such, the effects of the entangling and molecular contact areas should be kept separate.



**Figure 7** Schematic depictions of the various types of interactions that determine the specific joint strength in the contact zone between the fibres. Picture courtesy of Mats Rundlöf, AB Capisco.

The *diffusion* mechanism by which molecules from opposite surfaces migrate across the interface to create linkages between the surfaces, thereby increasing the adhesion, has also been suggested as a mechanism for joint formation between fibres [McKenzie 1984]. This suggestion was partly based on earlier research in which the acetylation of bleached eucalyptus pulp and forming the sheets in acetone was found to yield stronger sheets than those formed of untreated fibres prepared in water [McKenzie et al 1955]. A typical result from this investigation is shown in Figure 8.

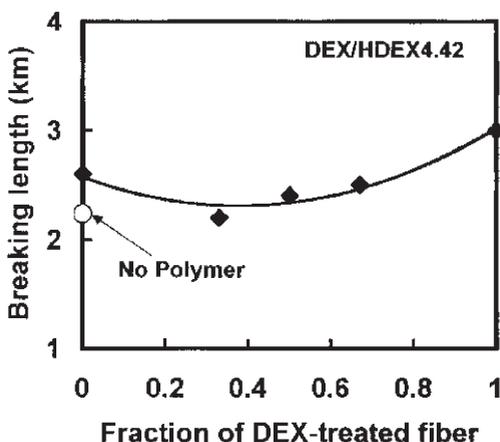
Based on these results McKenzie suggested that the acetylated fibre surfaces showed such a high degree of swelling that the molecules on their surfaces might migrate into adjacent fibre surfaces, creating strong fibre–fibre joints. Similar results have been achieved more recently via experiments in which the fibres were saturated with cationic dextrans, either with or without a hydrophobic substituent [Pelton et al 2000]. Despite the complete water solubility of both types of dextrans, mixing the dextrans resulted in the phase separation of water solutions containing these two polymers.



**Figure 8** Influence of acetylation of hydroxyl groups on the strength of sheets made from eucalyptus pulp at different degrees of substitution. Sheets were prepared either in water or in acetone under full-restraint drying. Adapted from McKenzie (1955).

Experiments with 50/50% mixtures of fibres saturated with either hydrophobic or hydrophilic dextrans resulted in a sheet that was weaker than sheets made from 100% of either fibre. These results were interpreted in terms of either a good mixing, or interdiffusion, of polymers in the external layers of the fibres, or a demixing when the polymers were incompatible with each other. Typical results are shown in Figure 9, which depicts the strength of papers made from different mixtures of fibres saturated with the two types of dextrans. HDEX and DEX in the figure correspond to hydrophobically modified dextrane and unmodified dextrane, respectively; the numbers in Figure 9 correspond to the properties of the hydrophobically modified dextrane, while C4 relates to a C4 fatty acid and 0.42 is the degree of substitution (DS) of the hydrophobic group.

In a recent investigation, Pelton (2004) also suggested that the hydrophilicity of the polymeric molecules attached to the fibre surfaces would improve the mixing of the molecules, thereby allowing for better interdiffusion of the molecules across the interface.



**Figure 9** Tensile strength as a function of mass fraction of DEX-treated fibres used in the preparation of the sheets. Adapted from Pelton (2000).

*Hydrogen bonding* is the molecular mechanism perhaps most commonly cited in explaining the development of molecular interactions in the fibre–fibre joint. The concept is appealing since it is well known that solvent water and hydroxyl groups on the fibre surface are both essential for the development of a strong fibre–fibre joint. This was demonstrated by McKenzie (1955) (see Figure 8), and the decrease in the strength of papers formed from water as the degree of acetylation was increased, was partly taken as a result of decreased hydrogen bonding between the fibres. A series of papers has also described how the hydrogen bonding between the fibres can be used to explain the development of the elastic modulus of the paper from interactions in the fibre–fibre joint [Nissan 1962a; Nissan et al 1962b; Nissan 1977].

However, several difficulties are encountered when discussing the development of hydrogen bonds between the fibres. First, no accepted theory is available that describes the co-operativity of many hydrogen bonds across an interface, comparable to the theories that describe van der Waals interactions. On the other hand, the van der Waals interactions are non-specific and long range, since there is a co-operativity of the van der Waals interactions with macroscopic bodies. The interaction energy,  $W_{vdW}$ , derived from van der Waals interactions with crossed cylinders can be described by Equation (4), where  $A$  is the Hamaker constant of the solid material in the cylinders,  $R_1$  and  $R_2$  are the radii of the cylinders, and  $D$  is the distance between the surfaces.

$$W_{vdW} = \frac{-A \sqrt{(R_1 R_2)}}{6D} \quad (4)$$

This equation shows that van der Waals interactions will develop between the surfaces at rather large molecular distances. There are, however, two important difficulties when evaluating the importance of these interactions: first, the cellulose will be waterswollen, which means that the Hamaker constant for dry cellulose will be difficult to apply directly in evaluating the interaction energy between the surfaces, and second, the Hamaker constant for *interactions* in water will be calculated by combining the Hamaker constant for water and, for example, for cellulose. Recent fundamental investigations have shown that van der Waals interactions are significant for interaction between cellulose surfaces at distances up to 40 nm, provided the electrostatic interactions are removed by low pH or high salt concentrations [Notley et al 2004]. It was found that by measuring the interaction between a cellulose sphere (radius 13.5  $\mu\text{m}$ ) and a flat cellulose surface (540  $\mu\text{eq/g}$  charge) in an aqueous NaCl solution (1 mM) at pH 3.5, it was possible to estimate the non-retarded Hamaker constant for cellulose in water to be  $9 \times 10^{-21}$  J [Notley et al 2004]. This is also in very close agreement with the Hamaker constant for cellulose in water as determined using spectroscopic measurements [Ödberg et al 1999], where the non-retarded Hamaker constant was found to be  $8 \times 10^{-21}$  J.

Since hydrogen bonding is specific, before such bonding can develop the surfaces have to come very close to each other and the orientation between OH groups on adjacent surfaces has to be precise. However, since fibre surfaces are very soft in water, with transverse moduli around 1 MPa, it is possible that the capillary forces exerted between the fibres as the fibre web is drying might pull the surfaces so close together that specific interactions might become possible. Since the fibre wall is highly swollen, the OH groups might also have enough mobility to orient themselves so as to allow for H bonding between the surfaces. However, it should be stated that there are no quantitative evaluations of the relative importance of hydrogen bonding to the development of strong fibre–fibre joints.

It has also been suggested [van Oss 1987] that the polar part of the interaction between two surfaces in water can be determined via a knowledge of the acid ( $\gamma^+$ ) and base ( $\gamma^-$ ) properties of the surfaces, and that the hydrogen bonding properties are included into these two terms. For two surfaces in contact, the work of adhesion between the surfaces can then be determined as

$$W_{12} = W_{12}^d + W_{12}^p = 2\sqrt{\gamma_1^d \cdot \gamma_2^d} + 2(\sqrt{\gamma_1^+ \cdot \gamma_2^-} + \sqrt{\gamma_1^- \cdot \gamma_2^+}) \quad (5)$$

where

$W_{12}$  = work of adhesion between surface 1 and 2 in contact

$W_{12}^d$  = van der Waals contribution to the work of adhesion

$W_{12}^p$  = polar contribution to the work of adhesion

$\gamma^d$  = dispersive part of the surface energy of a material

$\gamma^+$  = acid part of the polar part of the surface energy of a material

$\gamma^-$  = base part of the polar part of the surface energy of the material

Even though it is widely accepted that the van der Waals interactions can be calculated via the geometric average shown in Equation (5), it is still debated whether the polar interactions can be calculated according to the averaging procedure shown in Equation (5). If the method is correct, however, it would be a way to estimate the co-operativity of the hydrogen bonding capacity of a specific surface. This still remains to be proven, and since the  $\gamma^+$  and the  $\gamma^-$  properties of a specific surface are difficult to determine, it is difficult to critically test the validity of this approach.

The *electrostatic interactions* will naturally also make a significant contribution to the molecular interaction in the contact zone between the fibres. As for the other types of interactions, very few investigations are available in which the influence of the electrostatic interaction is quantitatively compared to other types of interactions. However, Stratton et al (1990) did determine the importance of different types of interactions for the joint strength between fibres via direct measurement of the joint strength of single fibre crosses. The focus of this investigation was to compare electrostatic interactions with covalent bonding, and the polymeric systems used for fibre treatments were

- 1) a combination between polydiallyldimethylammoniumchloride (P-DADMAC) and polystyrenesulphonate (P-SS). These are denoted D and S, respectively, in Table 2 – Only charge interactions between the fibres
- 2) a combination of a polyamideamineepichlorohydrine (PAE) condensate and carboxymethylcellulose (CMC). These are denoted A and C, respectively, in Table 2 – Covalent bonding also occurring between the fibres

From these results the authors concluded that the electrostatic interactions, D/S, were as efficient as covalent interactions, A/C, for the creation of strong joints, since the joint strength was even higher for the D/S system. However, considering the earlier discussion, many factors could affect the development

**Table 2** Summary of the influence of fibre type, fibre treatment (beating), and polymer treatment on the joint strength between the fibres, as determined by the mechanical testing of single fibre crosses. ml, represents the different degrees of beating (measured as standard freeness in ml) of a mixture of earlywood and latewood fibres. The bonded area was determined using a microscopy technique in which each fibre cross was measured. Adapted from Stratton (1990).

Fibre	Additive	Contact area ( $\mu\text{m}^2$ )	Joint strength ( $\text{N}/\mu\text{m}^2$ )
Earlywood		2410	2.1
Latewood		1500	6.4
Earlywood	A/C	3000	3.9
570 ml		2070	3.5
345 ml		2290	3.7
570 ml	A/C	2130	7.5
570 ml	D/S	2040	9.3

of joint strength in such treatments, and more clear-cut model experiments are needed before any quantitative ranking of different molecular interactions in the contact zone between the fibres can be established.

### **New techniques for the detailed description of the molecular interactions between fibre surfaces**

As concluded earlier, it is necessary to have better-defined systems for determining the relative importance of various molecular interactions in the contact zone between the fibres. In this respect, recent developments of both experimental methods and model systems representing the fibre surface have created new possibilities for these types of characterisation. To determine the detailed interaction between model surfaces it is necessary to employ highly accurate, high-resolution analysis techniques, and the development of the surface force apparatus (SFA) and the atomic force microscope (AFM) [see e.g. Claesson 1999] have opened up new possibilities. Furthermore, in combination with the development of well-characterised model cellulose surfaces [Holmberg et al 1997; Gunnars et al 2003; Fält et al 2003; Gray et al 2003], which are smooth at the nanometer scale, this will allow for elegant model experiments in which the importance of hydrogen bonding, van der Waals interactions, polymer diffusion, and electrostatic interactions may be studied.

Using the SFA in combination with Langmuir Blodgett (LB) films of cellulose, Holmberg [Holmberg et al 1997] was able to determine the work of adhesion between cellulose surfaces both in dry air and at 100% RH. In dry

air the measured adhesion force ranged between 500 and 1000 mN/m, and according to Equation (6) this corresponds to values of the interfacial energy of the cellulose surface between 53 and 106 mN/m. The difference was ascribed to the small-scale roughness that could still be detected on the LB films. In moist air, i.e. at 100% RH, the adhesion was difficult to measure due to the capillary condensation between the surfaces.

$$F/R = 3\pi\gamma_{sv} \quad (6)$$

where

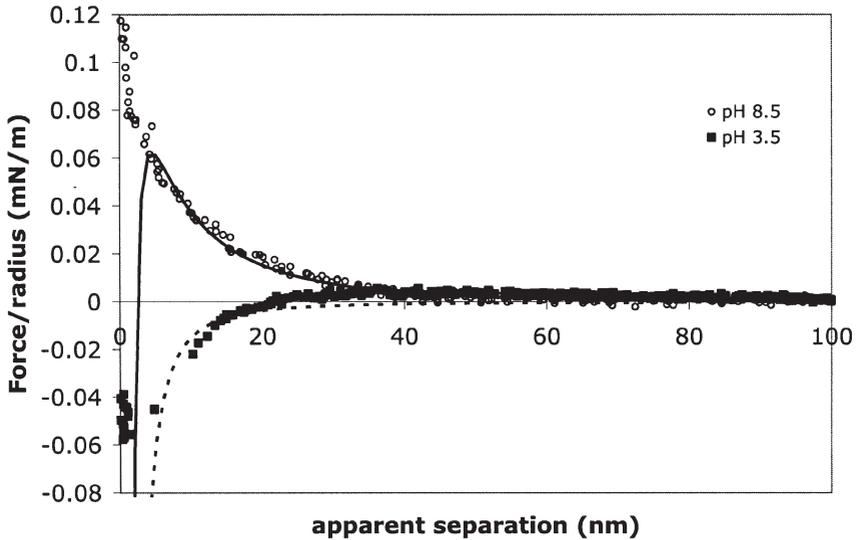
$F/R$  = force between the surfaces at pull-off, normalised with the radius of curvature of the system

$\gamma_{sv}$  = interfacial energy of the cellulose surface

With the LB films it was, however, difficult to investigate the true DLVO behaviour of the surfaces in water, due to steric interactions between the surfaces most probably arising from the highly swollen structure of the LB films [Österberg et al 2000]. However, in a recent AFM investigation [Notley et al 2004] in which spincoated (SC) cellulose surfaces were used together with a colloidal probe of cellulose, it was found that van der Waals interactions could be detected between the surfaces at low pH and that the interaction between the surfaces was dominated by electrostatic interactions at higher pH. This is depicted in Figure 10. The deviation from the theoretical prediction at pH = 8.5 is probably due to steric interactions between the surfaces.

All these results show that the new model systems and techniques can be used to study the detailed interaction between cellulose surfaces in both air and water, and that it is possible to determine the force–distance curves of such interactions.

Another approach to determine the adhesion between cellulose surfaces and cellulose surfaces coated with various types of additives is based on the Johnson, Kendal and Roberts (JKR) theory of contact mechanics between elastic surfaces [Johnson et al 1971]; this theory has recently been adapted to apply to cellulose systems [Rundlöf et al 2000]. In this approach, an elastic cap of crosslinked polydimethylsiloxane (PDMS), coated with a very thin layer of cellulose or some commonly used papermaking additive, is pressed against a model surface of cellulose; the radius of the contact zone between the two surfaces is then determined under various applied loads. By determining the relationship between the cube of the contact radius and the applied load, the work of adhesion between the surfaces can be determined by applying the JKR theory as described by Equations (7) and (8). Equation (8) shows how the pull-off force,  $F_{min}$ , also can be used to calculate the pull-off work of



**Figure 10** Surface forces on approach between a 509  $\mu\text{eq/g}$  charged cellulose surface and a 13- $\mu\text{m}$ -diameter cellulose sphere as a function of pH. Fits were performed on the data according to DLVO theory, pH 8.5 (solid line) and pH 3.5 (dashed line). The fitting parameters for pH 3.5 were  $\psi_0 = 0$  mV and a Hamaker constant of  $9 \times 10^{-21}$  J and for pH 8.5 were  $\psi_0 = -9$  mV,  $\kappa^{-1} = 30$  nm, and a Hamaker constant of  $9 \times 10^{-21}$  J. The fitting parameters assumed an identical surface charge for both cellulose surfaces. The scan size was 500 nm and the scan rate was 0.5 Hz. Forces were measured on approach in a background NaCl solution with a concentration of  $1 \times 10^{-4}$  M. Adapted from Notley and Wågberg (2005).

adhesion between surfaces when the surfaces are separated. This latter approach was also adopted by Holmberg et al (1997) using the SFA equipment.

$$a^3 = \frac{R}{K} (F + 3\pi RW + \sqrt{6\pi RW + (3\pi RW)^2}) \quad (7)$$

Where

$a$  = contact radius of the PDMS cap on the opposing surface

$R$  = radius describing the geometry of the system

For a hemisphere on a flat supporting surface it is equal to the radius of the cap

$K$  = elastic constant collected from fitting  $a^3$  against  $F$

$W$  = work of adhesion also collected from fitting  $a^3$  against  $F$

$$F_{\min} = -\frac{3}{2} \pi R W_{\min} \quad (8)$$

Based on earlier work [Mangipudi et al 1996], new equipment was especially designed to measure the adhesion between flat cellulose/hemicellulose/lignin surfaces and/or typical additives used in paper making [Rundlöf et al 2000]. A schematic representation of the equipment is given in Figure 11. By using a

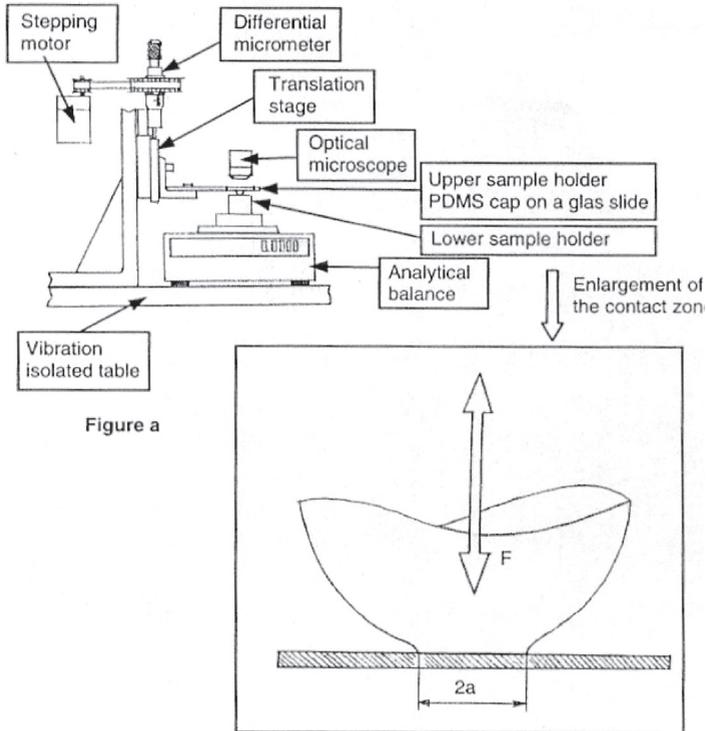
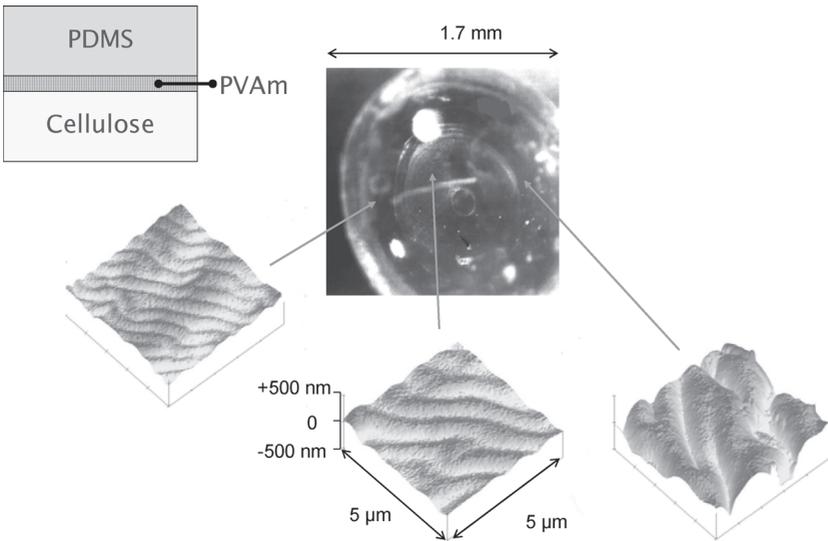


Figure a

**Figure 11** Schematic representation of the microadhesion measurement apparatus constructed to measure the interaction between, for example, cellulose surfaces or between cellulose surfaces and additives typically used in pulp and papermaking. Via a stepping motor that can be carefully controlled, a PDMS cap, used either as is or coated with a thin layer of a typical additive, is pressed against a model cellulose/lignin or hemicellulose surface. The load is measured using a high-precision balance, and the contact radius is determined using a CCD camera mounted on the optical microscope. The enlargement shows the load situation between the cap, typically 2 mm in diameter, and the model surface. Adapted from Rundlöf (2002a).

well-controlled application of load, measured using a high-precision balance, to the PDMS cap, and by measuring the contact radius from images collected using a CCD camera mounted on the optical microscope, it is possible calculate the work of adhesion by applying the JKR theory to the collected data.

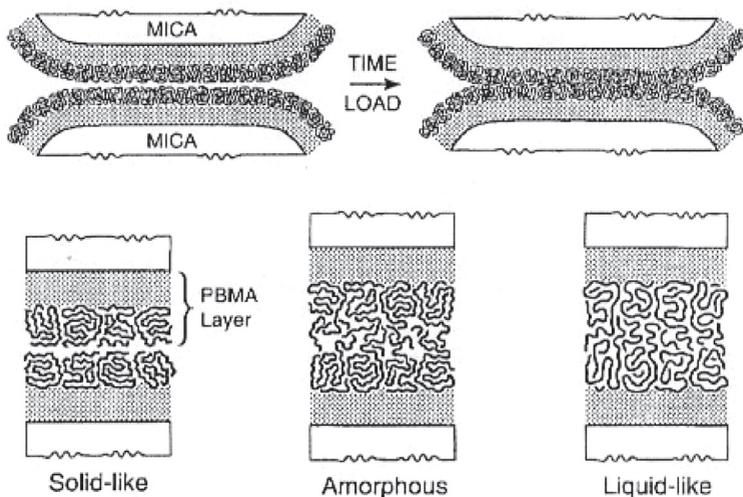
The methodology opens up many new possibilities for evaluating the interaction between typical surfaces in pulp and paper making. For example, it is possible to coat the PDMS cap with cellulose and measure the adhesion between two cellulose surfaces. By changing the time of loading and the relative humidity it is, for example, possible to evaluate the impact of molecular rearrangements on the cellulose surface on the adhesion and adhesion hysteresis between the surfaces. Another possibility would be to coat the cap with a typical papermaking additive and measure the adhesion and adhesion hysteresis existing between the additive and the cellulose surface; then this could be compared with the strength-enhancing property this additive has when used to treat fibres before sheet preparation. An example of this is



**Figure 12** Characterisation of different areas of the PVAm-coated PDMS cap after adhesion measurements against a model cellulose surface in air under ambient conditions. The insets in the figure show the AFM height images of the cap outside the area of contact during the measurements (far left inset), close to the centre of the contact (middle inset), and close to the area of changeover from a positive to a negative pressure on the cap (far right inset). Adapted from Rundlöf et al (2002b).

shown below, in which the cap was covered with either polyvinylamine (PVAm) or cationic starch (CS), and the adhesion and adhesion hysteresis between these additives and a model cellulose surface was then determined, using the equipment shown in Figure 11, under ambient conditions. TCF bleached chemical softwood fibres were then treated with either PVAm or CS, and laboratory sheets were prepared with the treated fibres. The results of these measurements are shown in Figures 12 and 14. Figure 12 presents AFM images of the PVAm-coated cap after adhesion measurements, and Figure 14, a) and b), present adhesion and paper strength data, respectively.

As seen in Figure 12, the structure of the PVAm layer is greatly dependant on where on the cap the AFM measurements are performed. The structure of the PVAm layer outside the area of contact reveals that deposition has not been ideal, and that there is slight unevenness of the PVAm layer. In the middle of the cap it is seen that the adhesion measurements have increased this unevenness, and this is even more obvious at the transition between the area of positive and negative pressure of the cap during measurement. These



**Figure 13** Schematic representation of how polymer molecules might migrate across the interface between the model surfaces to form strong adhesion. The figure is adapted from Israelachvili (1998) and represents the situation occurring when two polybutylmethacrylate surfaces, formed as 2- $\mu\text{m}$ -thick layers on mica supports, are brought into contact with each other. The state of the polymers, whether solid, amorphous, or liquid, mostly depends on the temperature and greatly affects how the molecules might migrate across the interface.

results are also in very good agreement with earlier measurements [Israelachvili et al 1998], made when the adhesion of thin layers (2  $\mu\text{m}$  thick) of polybutylmethacrylate was evaluated using SFA equipment. Structures similar to those presented in Figure 12 were found on the surfaces after the adhesion measurements. After measuring the time and temperature dependence of the formation of these structures, Israelachvili et al (1998) concluded that they were formed due to interdiffusion of the polymers across the interface between the polymers, as schematically described in Figure 13. The diffusion of the polymers across the interface is dependant on the contact time and the temperature and moisture conditions used during the measurements. The measured adhesion energy, determined in pull-off experiments, is dependant on how much time the molecules are given to mix and relax as the surfaces are brought together and separated, and these processes are hence not the type of equilibrium processes that can be described using the JKR theory. However, the experiments are highly repeatable and can be related to the type of polymer used and how the experiments are conducted.

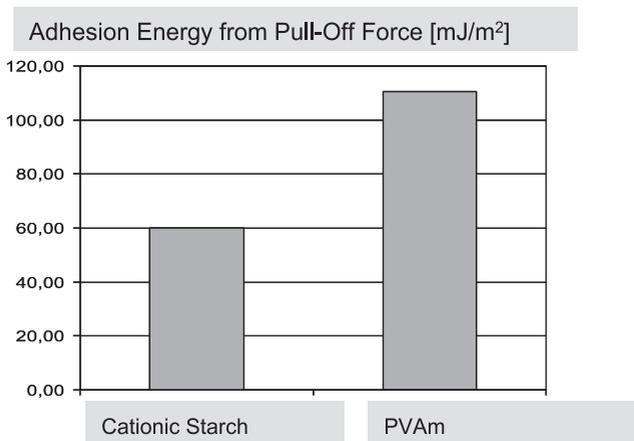
Based on these results, it may be suggested that the rims formed by the deposited PVAm layer during unloading are due to the stringing together of PVAm molecules that have migrated into the cellulose II model surface during contact. It should also be mentioned that the same patterns were not found after the starch experiments.

The results presented in Figure 14 were derived from the pull-off experiments with the polymer-coated PDMS caps. The adhesion energy revealed by the pull-off measurements of the PVAm is almost twice as large as that revealed by the measurements of the CS covered caps. Furthermore, as can be seen in Figure 14 b, this difference is also found for the sheet strength evaluation, indicating that there is congruence between how the adhesion between the surfaces develops and the efficiency of the additives in increasing sheet strength. Needless to say, this comparison is rather far reaching, and more work is needed; the results are included merely to show how model adhesion experiments can be used to clarify the working mechanism operating between different types of surfaces, and how this might help in developing new types of additives to increase or decrease adhesion between surfaces.

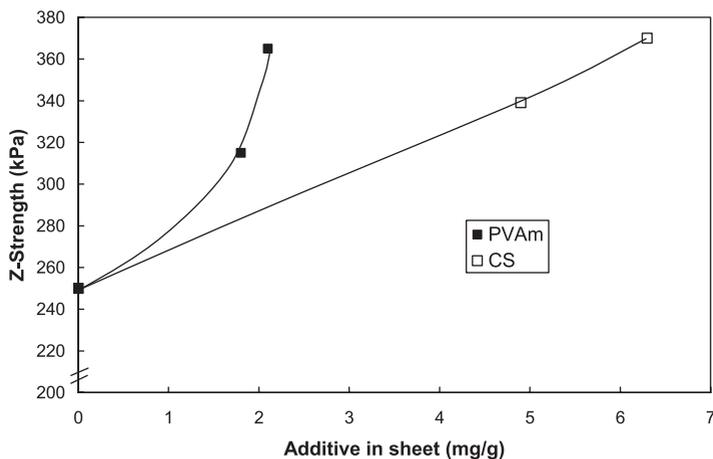
### **Correlation between joint strength and sheet strength**

After having established how experiments should be conducted so as to clarify the molecular mechanisms responsible for developing joint strength between the fibres, it is essential to establish how joint strength affects paper strength. In this respect it is important to characterize both the joint strength and the joined area between the fibres, in order to establish how different

a)



b)

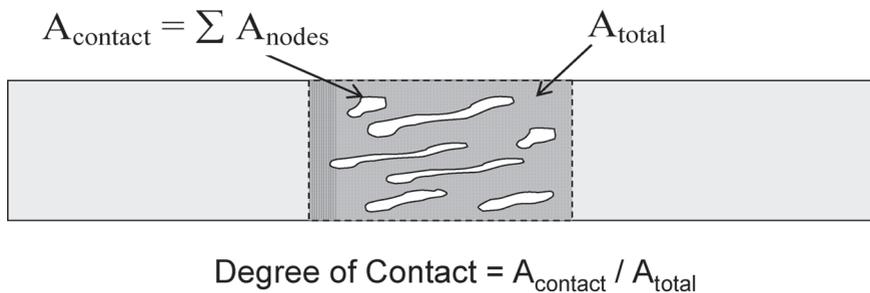


**Figure 14** a) Pull-off force data from the measurements of adhesion between PVAm- and CS-coated PDMS caps and model cellulose fibres. b) Z-strength measurements of sheets prepared from fibres coated either with PVAm or CS, as a function of the amount of additive in the sheet. Adapted from Rundlöf et al (2002b).

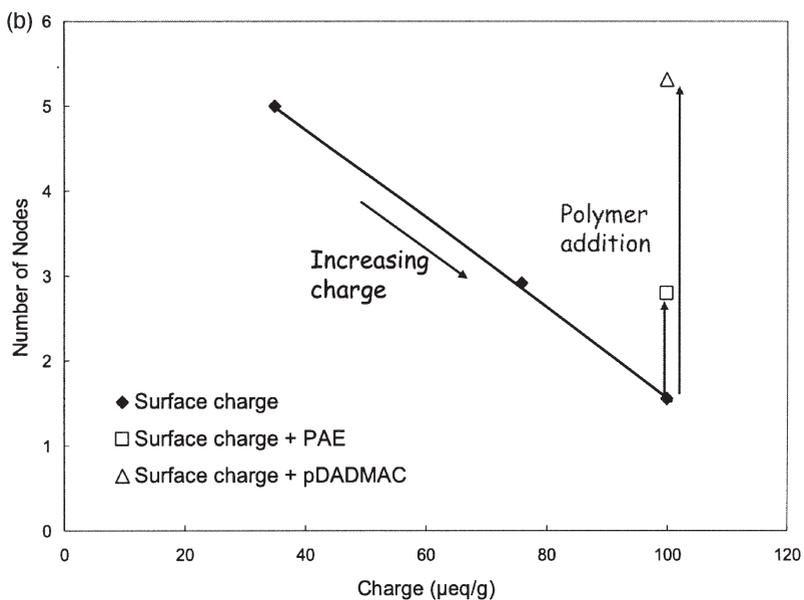
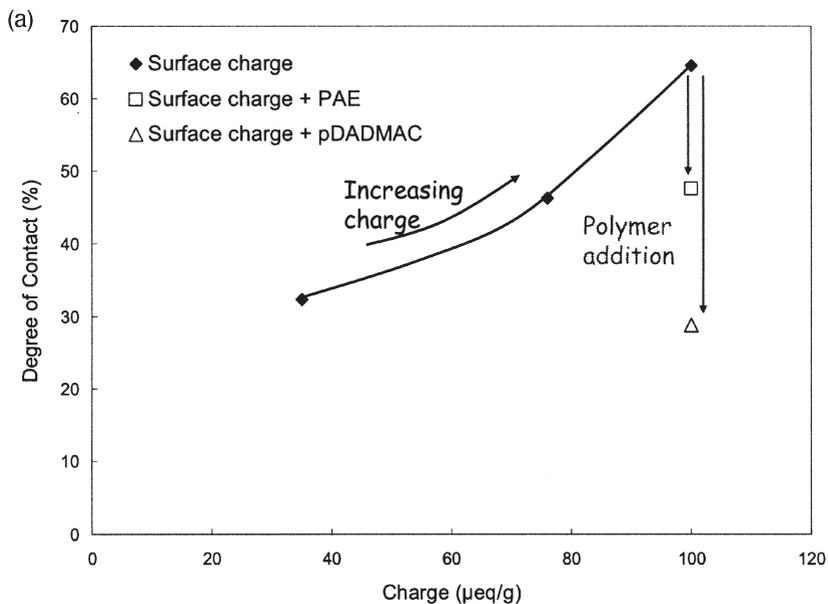
treatments will affect the molecular adhesion and the joined area between the fibres. Such measurements have received considerable attention over the years, and both the joined area between the fibres [Page et al 1962; Torgnydottir et al 2005] and the joint strength between the fibres [Schwiewind et al

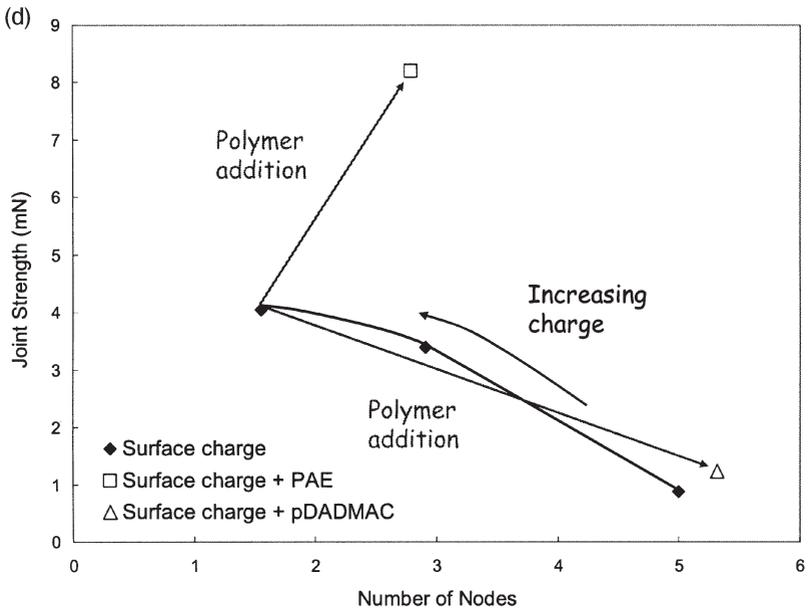
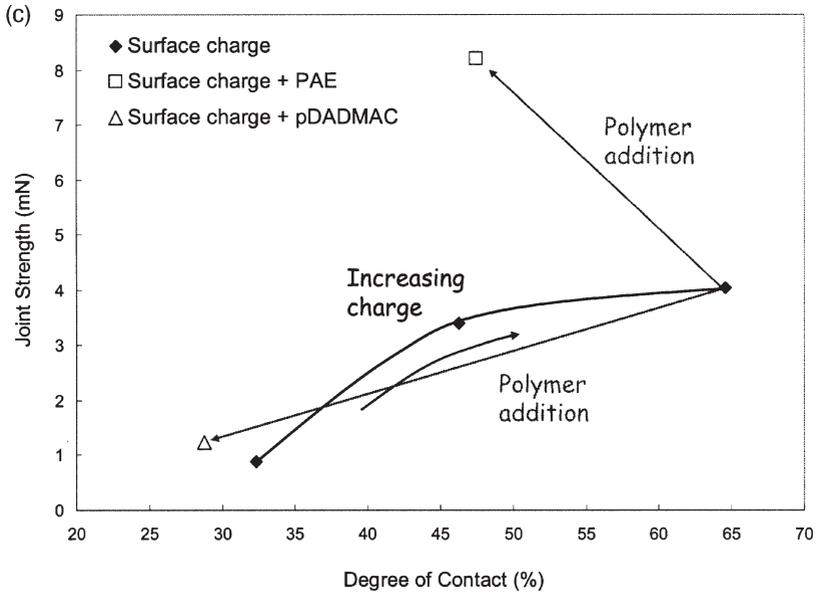
1964; Stratton et al 1990; Torgnysdotter et al 2004] have been estimated to determine how various treatments will affect these two entities. Recently, Torgnysdotter et al (2005) developed a technique in which the joint strength measurements of single fibre crosses were combined with a special staining technique for dried sheets in order to establish a link between the joined area, joint strength, and sheet strength. In the staining experiments, a dried paper was soaked in an acetone solution saturated with hexamethyl-P-Rosaniline chloride and then allowed to dry before it was separated to expose the contact zones. The main idea behind this evaluation method is that acetone will not disrupt molecular contacts between the fibres, so the dye will only reach molecularly non-joined areas between the fibres. By evaporating the solvent, the dye will be left only in the non-joined areas of the fibre cross; the joined areas will appear as non-dyed areas after fracturing the fibre–fibre joints in the paper. After separation, a typical disrupted contact between two fibres has the appearance depicted in Figure 15; as schematically shown in this figure, the degree of contact in the contact zone and the number of contact nodes can be defined from these measurements.

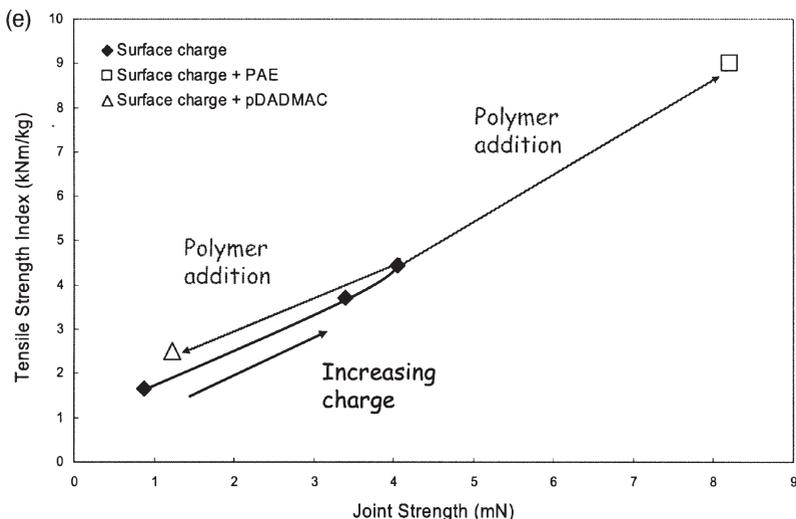
Model experiments using carboxymethylated rayon fibres treated with three different degrees of carboxymethylation investigated the influence of the charge and addition of various papermaking additives [Torgnysdotter et al 2005]. These measurements are included in Figure 16, a)–e), and are illustrative of how the various treatments affect the properties of the joined zone between the fibres, and of how the various additives affect the molecular adhesion between the fibres.



**Figure 15** Schematic representation of how the contact zone between two fibres can be characterised using a special staining technique in which a dried sheet is treated with an acetone solution of hexamethyl-P-Rosaniline. From the collected images, the degree of contact and the number of contact nodes was determined according to the figure. Adapted from Torgnysdotter et al (2005).







**Figure 16** Influence of surface charge and polymer addition on the development of the molecular contact area and the number of contact nodes in the contact zone between the regenerated cellulose fibres; the influence of these factors on both joint strength between the fibres and the strength of paper made from these fibres. The figures show the degree of contact (a) and number of nodes in the contact zone (b) as a function of charge of the fibres. Furthermore, the figures depict the relationship between joint strength and degree of contact (c) and the number of nodes in the contact zone (d), and between paper strength and joint strength (e). Adapted from Torgnysdotter et al (2005).

As can be seen in Figure 16, a) and b), charging the surface of the fibres increases the degree of contact and decreases the number of nodes in the contact zone. As expected, this also leads to an increase in the joint strength between the fibres, as shown in Figure 16, c) and d), since the molecular contact area between the fibres increases, and therefore the maximum stress in the contact zone will decrease under a certain applied load. Upon addition of a cationic polyelectrolyte, in this case polyDiMethylDiAllylAmmoniumChloride (P-DADMAC), and a typical wet strength agent, a polyamideamineepichlorohydrine condensate (PAE), there will be a deswelling of the fibres, or in this case, of at least the surface of the fibres [Swerin et al 1990]. As shown in Figure 16, a) and b), this in turn leads to a decrease in the contact area and an increase in the number of contact nodes between the fibres. However, as shown in Figure 16, c) and d), the PAE

addition increases the joint strength between the fibres, whereas the P-DADMAC addition significantly *decreases* joint strength. This difference between the polyelectrolytes was explained as being due to the different structures of the polymers [Torgnydottir et al 2005]. The PAE is commonly known to create covalent bonding with carboxyl groups on the fibres [Espy et al 1988; Wågberg et al 1993], so it can be concluded that the molecular adhesion increases much more than the contact area in the contact zone between the fibres decreases. P-DADMAC, on the other hand, has a hydrocarbon backbone that can only establish dispersive interactions with the cellulose surface, and apparently this is insufficient for the formation of a strong joint between the fibres.

From Figure 16, e) it is also evident that there is a linear relationship between joint strength and stress at break for these types of weak sheets. It is also evident from this figure that the complementary information obtained from contact zone analysis and adhesion measurements is absolutely necessary in order to draw any conclusions regarding the molecular action of different types of additives used in papermaking.

Finally, it should also be mentioned investigations similar to those described in Figure 16, a)–e), have been conducted for wood fibres [Forsström et al 2005], and the results of these investigations show the applicability of the technique to wood fibres as well. Since sheets from the wood fibres are stronger, it is difficult to arrive at the same linearity of the relationship between joint strength and sheet strength. However, contact zone analysis together with joint and sheet strength evaluation enables more firm conclusions to be drawn regarding molecular mechanisms, conclusions that are impossible to make using simple paper testing.

## DIFFERENT GROUPS OF DRY STRENGTHENING AGENTS

### Starch group

#### *Molecular structure*

Starches are the most important group of wet-end strength additives.

Starch is composed of two basic constituents, amylopectin and amylose. Depending on the source of starch, the relative amount of amylose may vary between zero percent (waxy maize) up to 30% for maize and wheat starches.

Amylose is a straight chain of  $\alpha(1-4)$ -linked glucopyranose units, whereas amylopectin has linear parts consisting of 20–30  $\alpha(1-4)$ -linked glucopyranose units joined in a branching manner by  $\alpha(1-6)$ -linked bonds. Amylopectin has an extremely high Mw ( $D_p = 2 \times 10^6$ ), whereas amylose has a lower Mw

( $D_p = 800\text{--}3000$ ) [see e.g. Banks and Greenwood 1975]. There are exceptions to these rules, and waxy maize starch, containing only amylopectin, has a significantly lower molecular weight than potato starch (Glittenberg 1993).

There are several authoritative reviews available on the use of starch as a dry strength resin [see e.g. Hofreiter 1981; Marton 1991; Reif and Gaspar 1980].

Unmodified starch has little or no substantivity to cellulosic fibres, although the amylose fraction may retrograde and precipitate onto stock particulates. While  $\beta(1\text{-}4)$ -glucans and  $\beta(1\text{-}4)$ -mannans may co-crystallise onto cellulosic surfaces (see below),  $\alpha(1\text{-}4)$ -glucans lack this ability. Therefore, almost all wet-end starches are cationic or amphoteric in nature.

The application and use of starches is a rather mature field. Interest in recent decades has focused on the use of amphoteric and cationic starches in microparticulate retention systems [see e.g. Hubbe 2004 and below].

#### *The adsorption of cationic and amphoteric starches onto wood fibres*

To evaluate the effects of starches on sheet properties, it is important to know how much starch was actually adsorbed.

The adsorption of cationic starch onto cellulosic fibres is well understood and was also reviewed by van de Steeg et al (1993).

Basically, the adsorption follows the general rules of the adsorption of cationic polyelectrolytes onto negatively charged surfaces. There is an optimum charge density for maximum starch adsorption, usually around a D.S. = 0.015–0.035, depending on fibre surface charge density and electrolyte concentration [Hedborg and Lindström 1993a; Retulainen et al 1993].

The adsorption increases slightly with electrolyte concentration, after which it decreases to zero adsorption at high electrolyte concentrations [Hedborg and Lindström 1993a; van de Steeg et al 1993]. The adsorption increases with both surface area (as more charged groups are accessible) and surface charge density [Marton and Marton 1976, Marton 1980; Retulainen et al 1993, Roberts et al 1986; Yoshizawa et al 1998].

The comparatively low charge density of most commercial cationic starches makes them vulnerable to interfering electrolytes. Hence, dissolved anionic substances and high cationic starches have come into more common use, often in conjunction with microparticles [Persson et al 1996]. The adsorption of starch onto fillers such as calcium carbonate is characterised by higher complexity, as non-ionic interactions play a prominent role in such adsorptive behaviour to fillers [Hedborg and Lindström 1993b].

Cationic starch may also be retained by precipitating non-self-retained starch by means of anionic polyelectrolytes or microparticles, such as

colloidal silica and bentonites [see e.g. Hubbe 2004], and aluminium hydroxide [Lindström et al 1989].

The use of amphoteric starches has achieved a certain popularity over recent decades [see e.g. McQuery 1990, Peek 1987; Sirois and Janson 1989], particularly in alkaline systems in the presence of colloidal alumina either from papermaker's alum or polyaluminium chlorides. It is essential that the negatively charged group is a phosphate group, as in potato starches. The key element is presumably the ability of colloidal alumina to form covalent bonds with phosphate groups. The system is essentially a microparticulate system showing strong dewatering features [Hedborg 1992; Lindström et al 1989].

Polyaluminium compounds and cationic polyelectrolytes also form complexes with anionic starches [Brouwer 1997] in a similar fashion, although cationic polyelectrolytes in conjunction with anionic starch do not produce the strong dewatering effects associated with microparticulate systems.

Another aspect of amphoteric starches is their self-association behaviour induced by mutual charge interactions between oppositely charged groups, inducing an apparently higher molecular weight of the starch [Glittenberg 1993].

#### *Mechanism of strength resin forcement by starch*

As discussed earlier, high molecular weight starch has better performance to enhance bond strength than low molecular weight starch [Brouwer 1997]. It has, for instance, been found that the molecular weight of potato starch is higher than that of waxy maize starch, resulting in higher bond strength [Brouwer 1997; Glittenberg 1993].

Whether amylose or amylopectin is a more efficient strength resin has been a contentious issue for years, and is still unresolved [Glittenberg 1993, Hofreiter 1981]. Starch dispersion has long been known to have a very significant effect on the strength performance of starches [see e.g. McKenzie 1965]. It is also unclear whether starches increase the relative bonded area or the specific bond strength.

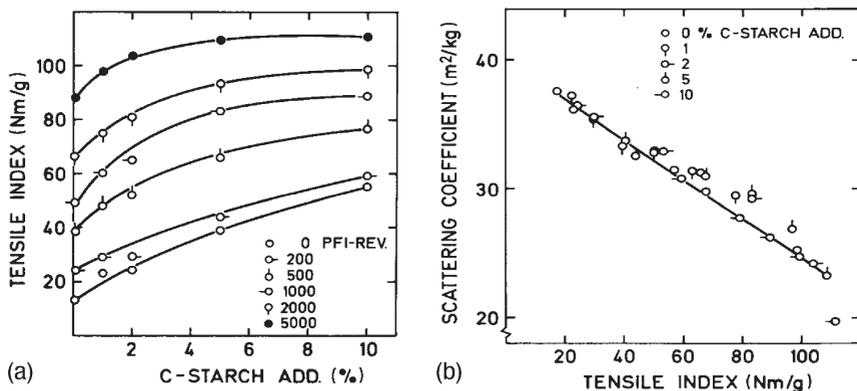
Hence, Moeller (1966) found that cationic starch is capable of increasing the strength of paper by contributing additional fibre–fibre bonds, instead of, or in addition to, merely reinforcing existing bonds. Gaspar (1982), on the other hand, found that specific bond strength was enhanced in the presence of starch. Howard and Jowsey (1985) arrived at the same conclusion. These authors also studied the effect of starch on fibre bonding to a glass surface, and found that the contact area increased, apparently contradicting the results of an earlier study of paper strength.

Few studies have investigated the effects of cationic starch charge density on strength properties. Interestingly, Retulainen et al (1993) found that low charge density cationic starch (D.S. = 0.009) improved strength more than higher charge density starches did (D.S. = 0.025–0.05). This indicates either that the conformation of starch on the fibre surface or that charge interactions play a role in strength improvement.

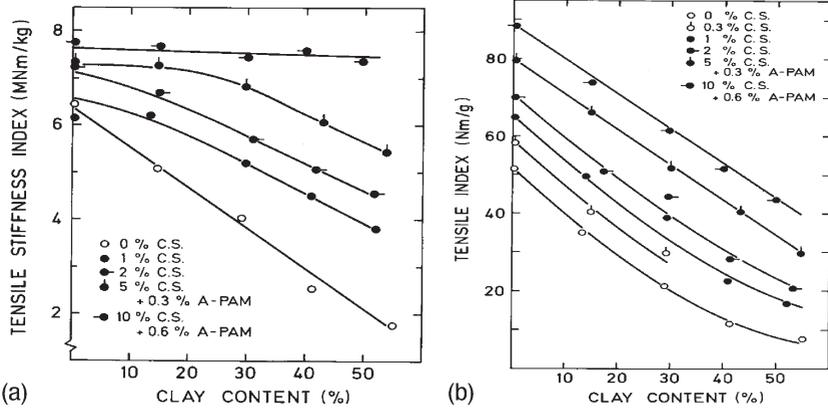
Again, caution is warranted regarding the effects of sheet forming procedures, as was illustrated by the studies of Roberts et al (1986, 1987). When studying the strength reinforcement effects of cationic starches, these authors showed that formation had a great effect on sheet strength.

Cationic starches contribute little to the tensile strength of papers made from groundwood pulps. The principal benefits of such starches are due to increased retention and Scott-bond internal strength [Hernandez 1970; Laleg et al 1991], and groundwood pulps presumably already have strong internal bond strength [Reynolds 1974]. Similarly, starches have rather slight effects on the strength of stiff fibres with low conformability [Retulainen et al 1993].

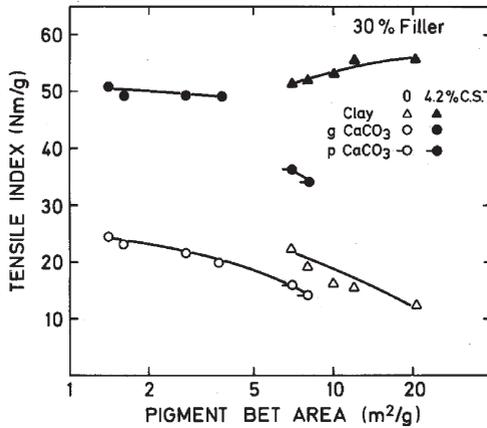
There is a general observation that starches cause greater strength improvement in weaker sheets (see Figure 17). This is, of course, exactly what would be expected from the theories of paper strength. A previously cited study [Lindström and Florén, unpublished] also found that properties such as the tensile strength–scattering coefficient and tear–tensile strength



**Figure 17** a) The effect of cationic starch on the tensile strength of bleached softwood kraft pulp beaten to different rev. in a PFI mill. b) The effects of beating and the addition of cationic starch on the tensile strength–scattering coefficient relationship [Lindström and Florén, unpublished data].



**Figure 18** a) The effect of cationic starch on the tensile strength of clay-filled papers. b) The effect of cationic starch on the tensile stiffness index of clay-filled papers [Lindström and Florén 1984].



**Figure 19** The effect of cationic starch on the tensile strength of filled papers with various specific surface areas of filler [Lindström and Florén 1987].

relationships were invariable properties, regardless as to whether strength was increased by beating or starch addition. This was somewhat unexpected and would suggest that beating and starch addition act in a similar way.

Starches have a very strong reinforcement effect on filled papers [Lindström et al 1985; Lindström and Florén 1984, 1987]: the higher the filler content, the stronger is the strength improvement, as depicted in Figure 18. Unlike in unfilled papers, the elastic properties are also significantly improved, as depicted in the figure. The effect of starch addition is more accentuated the larger the specific area of the filler, as shown in Figure 19.

It has also been shown [Lindström et al 1985] that in addition to improving sheet consolidation, starches release stress concentrations during sheet consolidation through a stick–slip mechanism. Figure 20 illustrates how stress concentrations, as determined by Zhurkov type life-length experiments, are greatly decreased by the addition of cationic starch to filled papers (though to a much lesser extent in unfilled papers).

In conclusion, cationic starches may improve strength by at least the following three traditional mechanisms:

- Improving sheet consolidation—increased bonded area, as determined by the scattering coefficient, resulting in increased sheet density
- Increasing the specific bond strength
- Decreasing stress concentrations in paper sheets

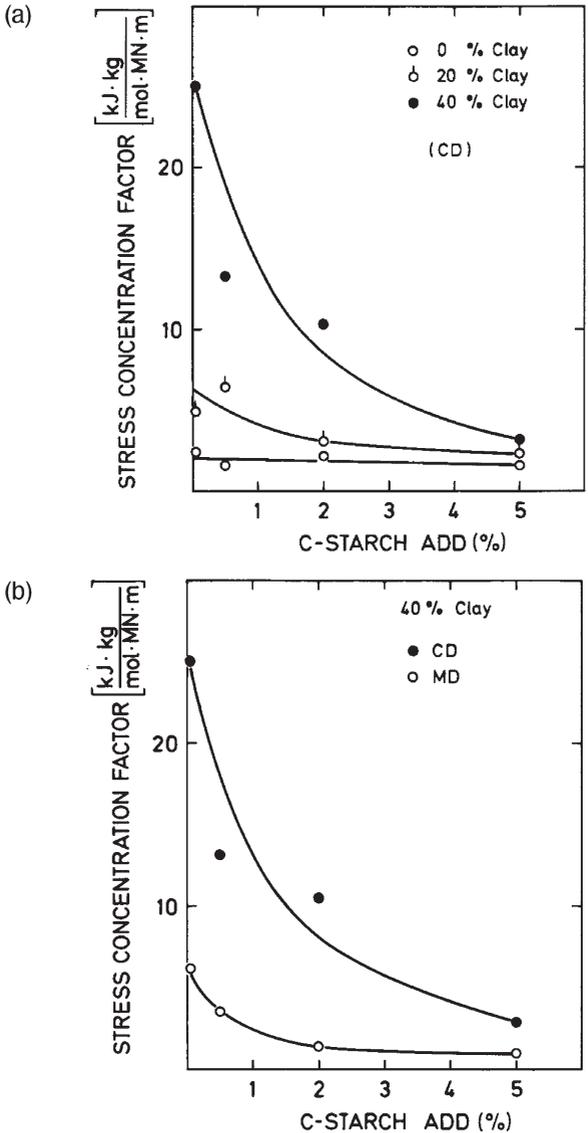
## **Acrylamide – based polymers**

### *General*

Acrylamide-based dry strength resins were developed in the late 1950s [Swift 1957]. Most of the development work was conducted during the 1960s, and this work has been reviewed by Reynolds (1980) and Reynolds and Wasser (1980). Since these reviews, little work has been done apart from that of Tanaka's group in Japan [e.g. Suzuki and Tanaka 1977; Tanaka and Senju 1976a; Chen and Tanaka 1994]. Two reviews have also been written by the same author [Tanaka 1994, 1995].

The market share of polyacrylamides (PAMs) has yielded in favour of cationic starches, except on the Japanese market, where PAMs have been competitive for economic reasons [Reynolds 1980].

Acrylamide can be copolymerised with a host of different monomers, such as acrylic acid, vinyl pyridine, 2-aminoethyl methacrylate, diallyl-dimethyl-ammonium chloride, dimethyl-amino-propylacrylamide, and diamine ethyl acrylate, styrene, and such copolymers have been used in various dry strength formulations.



**Figure 20** The effect of the addition of cationic starch on the stress concentration factor of papers with various clay filler levels. A) Crossmachine direction (CD). b) Comparison between machine direction (MD) and crossmachine direction (CD). [Lindström et al 1985].

It was recognised early on [Linke 1962] that high  $M_w$  PAMs were superior to low  $M_w$  PAMs, although excessive flocculation caused by the use of high  $M_w$  PAMs impairs formation resulting in weaker sheets.

### *Adsorption of acrylamide – based polymers onto wood fibres*

The first PAMs introduced were anionic copolymers with acrylic acid, and early research focused on retaining these polyelectrolytes with alum. Later on, cationic polyacrylamides (C-PAMs) were introduced, and the adsorption behaviour of C-PAMs onto fibres is well understood in terms of modern polyelectrolyte theories [see e.g. reviews by Lindström 1989; Wågberg 2000].

Many innovative formulations were also developed, such as dual polymer addition systems, acid formulations with anionic and cationic PAMs which form polyelectrolyte complexes by precipitating onto the fibre surfaces when subjected to a pulp suspension, and PAMs with specific affinity for lignin-containing pulps by incorporation of hydrophobic monomers making the PAMs more hydrophobic [Reynolds 1980]. The latter idea has also been further developed, but now in the area of retention aids [e.g. Persson et al 1999; Struck et al 1999; Klemets et al 1999].

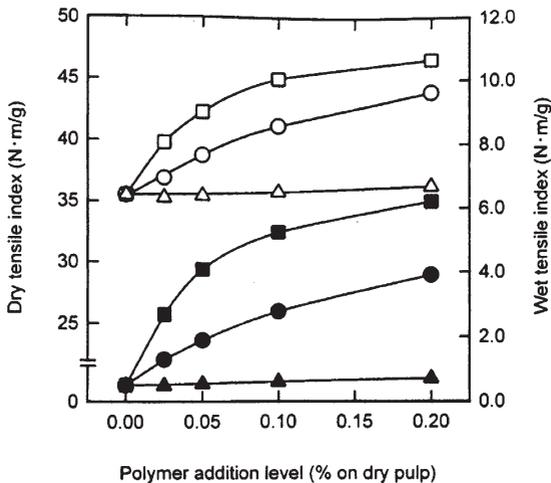
Alluding to more recent developments, a novel and different way to introduce PAMs into paper sheets has also been explored. Kitaoka and Tanaka (2001) separated the cellulose-binding domain (CBD) of commercial cellulase and covalently linked the CBD to anionic polyacrylamide using papain. The CBD-A-PAM adduct was, however, found to be inferior to a polyamideamine-epichlorohydrin (PAE) resin (see Figure 21).

### *Mechanism of action of PAM*

The overall strength improvement pattern for PAM is similar to that of starch derivatives. The largest improvement is in internal bond strength, whereas the modulus is only slightly affected [see e.g. Carlsson et al 1977]. There is either no increase [Reynolds 1974] or only a slight increase in sheet density – in any case, much less than the increase in sheet density occurring during beating, if compared at the same tensile strength level [Yamauchi and Hatanaka 2002].

## **Chitosan**

Chitosan is a high molecular mass linear carbohydrate composed of  $\beta(1-4)$  linked 2-amino-2 deoxy-D-glucose units, prepared by the hydrolysis of the N-acetyl groups from the natural polymer, chitin. Chitin is a major structural component of many creatures, including crustaceans and insects. Crab and



**Figure 21** Tensile strength index of handsheets prepared with cellulose-binding domain-anionic polyacrylamide (circles), A-PAM (triangles), or polamideamine-epichlorohydrin (squares). Open and filled symbols indicate the dry and wet tensile indices, respectively [Kitaoka and Tanaka 2001].

shrimp wastes are abundant sources of chitin [Muzzarelli 1985]. It has long been known that chitosan is an excellent binder for cellulosic fibre structures [see e.g. Allan et al 1972, 1975, 1977]. On a weight basis, chitosan has been found to be 40% more effective than starch [Allan et al 1977]. Chitosan not only gives dry strength to paper, but is also an efficient wet strengthening agent. However, its isolation and hydrolysis is time consuming, and the polymer is expensive and hence has not been significantly commercially exploited in the paper industry.

Chitosan's close stereochemical similarity to cellulose suggests that chitosan-cellulose combinations should have some interaction. However, experimental observations are not very supportive of this hypothesis, as discussed below.

The amino groups of chitosan become protonised under acidic conditions and the polymer becomes soluble. Deprotonised chitosan is not soluble under alkaline conditions. The adsorption of chitosan onto cellulose is governed by charge interactions at acidic pH values, and under alkaline conditions the polymer is precipitated onto cellulosic fibre surfaces. Adsorption therefore increases at higher pH levels [see e.g. Domszy et al 1975].

Chitosan is more effective the higher the  $M_w$  of the polymer [Allan et al

1977], and the fully deacetylated version of the polymer is most efficient with respect to its dry strengthening effects [Allan et al 1975].

High  $M_w$  chitosan is also a strong flocculant, which may hamper its dry strengthening effects by impairing sheet formation. This was recognised early on, and it was found that spray deposition was the most effective deposition mode [Allan et al 1977].

More recent investigations by Laleg and Pikulik (1991a, 1992, 1993a) have found that chitosan is an efficient agent to enhance wet web strength. On chemical pulps, the wet breaking length increases with the addition of chitosan, whereas chitosan has no effect on the wet breaking length of mechanical pulps. On the other hand, chitosan has a very significant effect on improving the wet stretch to failure for mechanical pulps.

The working mechanism of chitosan is, however, elusive [Allan et al 1977; Laleg and Pikulik 1992].

Basically, chitosan may interact in at least three different ways: through hydrogen bonding interactions with cellulose, through charge interactions, and through covalent bonding. Wet strength is only obtained at pH values higher than  $\text{pH} = 5$ , and it has been suggested that the primary amino groups may react with aldehyde groups to form Schiff bases [Allan et al 1977; Laleg and Pikulik 1992]. Although chitosan is an efficient wet strength resin, it does not equal the performance of commercial polyamideamine epichlorohydrin resins [Niekraszewicz et al 2001].

Chitosan is an efficient dry strength agent under both acidic and alkaline conditions [Lertsutthiwong et al 2002], although alkaline deposition was less efficient than acidic deposition (based on the same amount of chitosan in the sheet). This may be explained in at least two ways: adsorption provides a better chitosan distribution than precipitation does, and/or dry strength is promoted by the ionic interaction between the cationic chitosan and the anionic fibres – as suggested by early investigations of chitosan [see e.g. Allan et al 1977].

As chitosan is also an efficient dry strength agent for mechanical pulps, stereoregular hydrogen bonding does not seem to be the governing mechanism, unless the strengthening mechanism differs between chemical and mechanical pulps.

## **Gums**

### *General*

The use of various gums was extensively studied at the Institute of Paper Chemistry after the Second World War by Swanson and co-workers [e.g.

Swanson 1950, 1956, 1961]. At that time, unmodified gums with a natural affinity for cellulosic fibres were used by the industry. The introduction of cationic starches has thereafter dominated as the commercially important dry strength adjuvant, although cationic gums are available in the marketplace.

An extensive literature examines the various gums [see e.g. reviews by Baird 1994; Davidson 1980; Werdouschegg 1980; Whistler and Bemiller 1973]. More recently there has been interest, not so much in the working mechanism of gums, but more related to their interaction with cellulosic surfaces. It was recognised early on [Gruenhut 1953] that the stereochemistry of mannans was similar to that of cellulose, and this provided a means by which the adsorption onto cellulose could be understood. There has also been recent interest in the release and resorption of mannans onto cellulosic surfaces [Hannuksela et al 2004; Hannuksela and Holmbom 2004].

A situation similar to that of the mannans pertains to the affinity of glucans for cellulosic surfaces. A study of the adhesive properties existing between various glucans and cellulose I and II revealed that xyloglucan, locust bean gum (LBG), chitosan, and  $\beta(1-4)$ -glucan showed a strong affinity for both cellulose I and II. The mechanism of interaction was assumed to be based on the complementarity of the surfaces of these 1-4 linked  $\beta$ -glucans [Mishima et al 1998].

Papermakers have known of the dispersion power of gums since ancient times; there are, however, few publications dealing with this issue. In this context, the publication by de Roos (1958) is a landmark study. It investigated a number of polysaccharides in order to evaluate the fibre dispersing power of these additives. The study concluded that methylcellulose, ethylhydroxyethylcellulose, carboxymethylcellulose, locust bean gum, and guar gum were efficient dispersion agents, and that tamarind gum, pectin, alginate, and starch ether disperse less well, and that konnyaku, mesquite, gum arabic, dextrin, dextran, and carrageenin do not disperse at all. The field of fibre dispersion has also been reviewed recently by Rojas and Hubbe (2004).

It is obvious that polysaccharides with  $\beta(1-4)$ -mannan and  $\beta(1-4)$ -glucans in the main chain are the most efficient dispersants. Although the authors did not investigate the adsorptive properties of these polysaccharides, it is obvious from the above discussion that such polysaccharides have an affinity for cellulosic surfaces. Gums are seldom used as dispersants today, mainly because their adsorption is seldom quantitative, and this is not compatible with modern papermaking that uses closed papermachine systems. It is most likely that their dispersing power is related to a decreased fibre–fibre friction [see e.g. Mason 1950], and if cationic polysaccharides are used, they act as flocculants rather than dispersants.

Efficient dispersants are greatly needed in modern papermaking and our laboratories are reinvestigating the issue.

*Locust bean gum*

Locust bean gum (LBG) is produced from the endosperms of the seeds of the carob tree (*Ceratonia siliqua*). LBG is similar to guar gum, being a linear galactomannan built up of (1-4) linked  $\beta$ -D-mannopyranosyl units in the main chain. The side chains are single  $\alpha$ -D-galactopyranosyl units attached to the main chain with 1-6 linkages. The side chains are probably unevenly distributed on the main chain, and the polysaccharide can therefore be considered a natural block polymer [Davidson 1980]. The mannose:galactose ratio is higher for locust bean gum (3:1-6.1:1) than for guar gum (2:1) [Werdouschegg 1980].

The sorptive characteristics of LBG were studied in the 1950s and 1960s [e.g. Gruenhut 1953; Leech 1954; Russo and Thode 1960]. The adsorption increases with temperature [Russo and Thode 1961], appears to be irreversible [Leech 1954], and is specific to cellulosic surfaces. Galactomannan is adsorbed onto bleached and unbleached kraft pulps but not onto mechanical pulp surfaces [Ishimaru and Lindström 1984].

Suurnäkki (2003) found that the adsorption of locust bean gum galactomannan onto BKP depends on both the D.S. and the molecular weight of the adsorbed mannan. However, this dependency was opposite to that of guar gum galactomannans [Hannuksela et al 2002]. This may be explained as a difference in the galactomannan structure of the two gums.

Recent studies of the interaction between LBG and cellulose crystallite surfaces show that most mannosyl residues of the mannan backbone [Newman and Hemmingson 1998], not just the small portion contained in long segments, which lack galactose residues, are involved in the interaction. Use of  $^{13}\text{C}$  NMR has revealed that unsubstituted mannan segments can bind to cellulose by undergoing a conformational transition to an extended 2-fold form [Whitney et al 1998]. Cellulose crystals have also been shown to act as seed crystals for the crystallisation of ivory nut mannan, which has been shown to crystallise in a shish-kebab type of morphology onto cellulose fibres [Chanzy et al 1978].

Many studies have examined the effects of locust bean gum on paper strength, ranging from the classic studies by Swanson (1950) and Leech (1954) to the more recent study by Suurnäkki (2003).

### *Tamarind gum*

Tamarind gum is extracted from the seeds of the *Tamarindus indica* tree. The kernels of these seeds are used to produce tamarind kernel powder (TKP), which contains many different substances such as polysaccharides, proteins, fibres, fats, and inorganic salts [Whistler and Bemiller 1973; Gerard 1980]. The polysaccharide in TKP is a slightly branched xyloglucan (Xg). Xg is a non-ionic polymer, composed of  $\alpha(1-6)$ -D-linked xylosyl residues along a  $\beta(1-4)$ -D-glucopyranosyl backbone, and having important biological functions in the cell wall of plants [Hayashi 1989]. Because of its important biological functions, there has been recent interest in this polymer, also on issues related to paper manufacture.

Depending on the source of Xg, the xylose residues can be further substituted with galactosyl and fucosyl residues.

Xg has been found to adsorb strongly to cellulose surfaces, such as bacterial cellulose and microcrystalline cellulose [e.g. Mishima et al 1998; Hayashi et al 1987, 1994; Vincken et al 1995], and also to cellulosic fibre surfaces [Molinariolo 1989; Christiernin et al 2003; Brumer et al 2004]. The binding of Xg to cellulose occurs with the backbone  $\beta(1-4)$ -D-glucan chain having a complementary conformation to cellulose [Taylor and Atkins 1985]. Temperature and pH do not have a marked effect on adsorption, but there might be a certain pattern of galactosyl substitution, which is related to a higher Xg-binding affinity [de Lima et al 2001].

Recent investigations [Christiernin et al 2003; de Lima et al 2001, 2003] have shown that Xg enhances the strength properties and formation of paper [Christiernin et al 2003; Yan 2004]. The improved formation of paper is related to the decreased friction between wet fibres promoting fibre dispersion.

Because of the strong sorption of Xg onto cellulose, Xg can be used as a target molecule to provide functional groups on cellulosic surfaces. Xg modification using chemoenzymatic (using xyloglucan endotransglycolase) modification has been demonstrated [Brumer et al 2004].

### *Guar gum*

Guar gum is extracted from two plants, *Cyamopsis tetragonolobus* and *Cyamopsis psoraloides*. The gum is mainly composed of a nonionic polysaccharide built up of the two sugars, mannose and galactose (e.g. a galactomannan). The ratio between these sugars is normally approximately 2:1 (mannose: galactose). The polysaccharide has a linear main chain built up of  $\beta(1-4)$ -linked D-mannopyranosyl units. The main chain has side chains of

single  $\alpha$ -D-galactopyranosyl units attached to every second mannopyranosyl unit on the main chain with 1–6 linkages [Davidson 1980].

The sorption of galactomannan onto chemical pulps is related to the interaction between the mannan chain segments and cellulosic surfaces. The sorption of galactomannan onto bleached kraft pulp appears to be unaffected by temperature, pH – although Keen and Opie (1957) did report a pH dependence – and electrolytes, and the sorption appears to be irreversible [Hannuksela et al 2002].

The structure of the galactomannan polysaccharide does affect the sorption. It was found early on that the enzymatic hydrolysis of guar gum yielded a galactomannan with a higher mannose:galactan ratio. This decreases the solubility and increases the adsorption of guar gum onto fibres [Dugal and Swanson 1972].

A lower degree of side chains also enables the backbone to come closer to the cellulose chain, which increases the adsorption. This, combined with the fact that glucose (cellulose chain) and mannose (galactomannan chain) have almost identical conformations, could support the theory that galactomannan and cellulose can co-crystallise [Hannuksela et al 2002; Hannuksela et al 2003; Hannuksela and Holmbom 2004].

GMs enhance strength, decrease tear, increase tensile strength, increase WRV and SR, and improve formation. An intermediate galactose content produces the optimal strength increase [Hannuksela 2004].

## **Wood hemicelluloses**

### *Galactoglucomannans*

The sorption of mannans onto various fibre surfaces was recently reviewed by Hannuksela and Holmbom (2004).

Softwood mannans are galactoglucomannans (GGMs) composed of (1-4)-linked  $\beta$ -D-mannopyranosyl units alternating with some (1-4)-linked  $\beta$ -D-glucoopyranosyl units. Varying amounts of (1-6)-linked  $\alpha$ -D-galactopyranosyl are found as single side groups. Softwood GGMs are also partly acetylated in positions 2 and 3 of the mannose units.

GGMs adsorb strongly onto BKP and cotton. Sorption also increases with increasing deacetylation [Laffend and Swenson 1968a; Hannuksela et al 2002] and temperature [Clayton and Phelps 1965].

Deacetylated GGM has better strength performance than acetylated GGM does [Laffend and Swenson 1968b]. Acetylated GGM is only adsorbed onto chemical pulps and not onto mechanical pulps [Hannuksela et al 2003]. Again, deacetylated GGM adsorbs better. Bleaching of mechanical

pulps induces deacetylation [Sundberg and Holmbom 2004]. The result is that GGMs, released from mechanical pulps during refining, are reabsorbed onto the reinforcing pulp, which is usually a bleached kraft pulp.

A comparison was made early on between various hemicelluloses regarding their impact on paper strength. Higher mannan contents were shown to produce greater strength improvements approaching those of locust bean gums. Arabogalactans were also shown not to contribute to strength [Thompson et al 1953]. Again this points to the importance of the interaction of (1-4)-linked  $\beta$ -mannoseyl units with cellulose.

### *Glucuronoxylans*

Softwoods contain arabino-4-O-methylglucuronoxylan, which is substituted on average by one 4-O-methyl-D-glucuronic acid group per five or six D-xylose units. In hardwoods, the xylan is O-acetyl-4-O-methylglucuronoxylan. On average every tenth xylose unit is substituted by a 4-O-methylglucuronic acid residue, and the number of acetyl groups is 3.5–7 per ten xylose units [Schimitzu 1991].

It has long been known [e.g. Axelsson et al 1962; Hansson and Hartler 1969; Hartler and Lund 1962; Yllner and Enström 1956, 1957] that wood xylan is extensively modified during the kraft cook. At the end of the cook some of the dissolved xylan is reabsorbed onto the fibres, and several investigators have studied the processes occurring during kraft cooking. Furthermore, the methylglucuronic groups of xylan are almost completely converted to hexeneuronic acid groups during pulping [e.g. Buchert et al 1995].

Reduction or protonisation lowers the solubility of glucuronoxylans (or decreases the repulsion between anionic surfaces and anionic xylans) [Walker 1965]. More recent studies [Mitikka-Eklund 1996] have also confirmed that a higher ionic strength or lower hydroxyl ion concentration increases sorption. The xylan in solution has a less ordered state than the adsorbed xylan does. Furthermore, xylan adsorbed onto pulps tends to adopt the same two-fold axis conformation as cellulose has, which requires a strong interaction between cellulose and xylan chains.

The tensile strength improvement has also been reported to be related to the fibre charge after precipitation of the glucuronoxylan [Schönberg et al 2001].

### **Latex additives**

The potential advantage of using latex additives has long been recognised but seldom exploited in commodity paper products. Moreover, latex products are

recognised as multifunctional, not only substantially improving dry strength, but also wet strength and water repellence [Alinec 1999].

In a series of papers, Alinec, either alone or in collaboration (1976, 1977a, 1977b, 1982, 1985, 1991, 1999, 2000), has investigated the effects of various cationic latexes on paper properties.

A prerequisite to improving strength is that the latex should be film forming. However, the various film-forming styrene-butadiene latexes produce similar strength improvements, despite the fact that their film properties are quite different. Hard, pure polystyrene latex with a high  $T_g$  (105°C) interfered with bonding, unless the sheet was heated at a higher temperature. Particle size distribution was critical and the deposition of the cationic latex in the hetero-coagulation mode produced superior results with respect to the reinforcement power of the latex. On the other hand, Engman et al (1976) found that spraying polymers into the web improves the use of the polymer in the stress transfer process.

The latex increases not only the tensile strength, but also the strain to break. Heating is important in bringing about the coalescence of the latex in the sheet and in inducing the oxidation of the double bonds in the latex, which stiffens the latex and improves the overall strength of the paper.

Alinec (1999) has speculated that the role of the latex is to fill in the areas of surface roughness; this provides a larger area for molecular contact between the fibres and improves the stress transfer between the fibres. Alinec also concluded that as long as the polymer adheres to the fibres in amounts sufficient to fill but not exceed the depressions comprising the surface roughness, the mechanical properties of the polymer are less important than those of the fibres in improving the bonding.

Interestingly, the latex provided a means by which the tensile strength could be increased without affecting the scattering coefficient [Alinec 1991], in spite of the fact that the non-bonded surface area (through  $N_2$  adsorption) decreased with the increased sheet loading of the latex.

Alinec and Lepoutre (1982) investigated soft and stiff butyl acrylate-styrene latexes, a soft butyl acrylate-methylacrylate latex, and a soft ethyl acrylate-styrene latex for use as dry strength resins. The authors noted that the latexes had no significant effect on unfilled (clay filler) papers, but a significant effect on clay-filled papers. Such a comparison points to the importance of the specific molecular structure of the latex.

## **Some recent developments in the field of dry strength additives**

### *Carboxymethylcellulose grafting (CMC)*

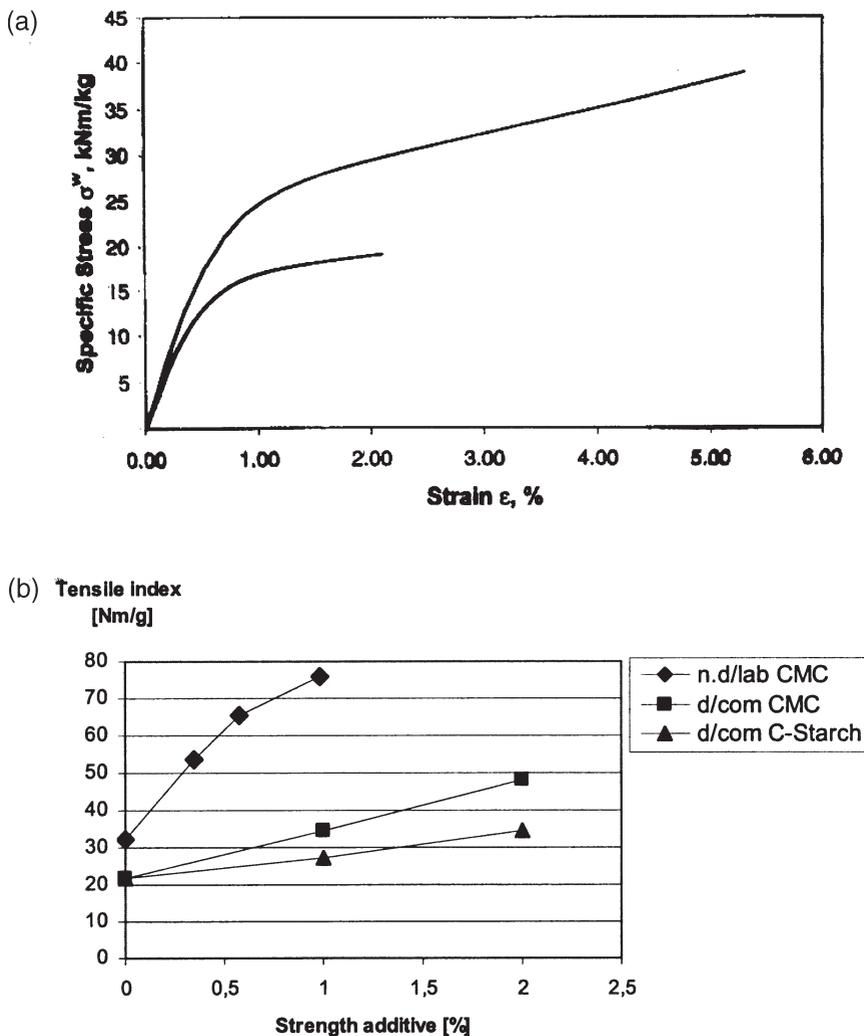
Carboxymethylcellulose (CMC) has long been known as a paper strength additive, primarily used for surface sizing, but also as a wet-end additive, if combined with suitable cationic additives. CMC is often combined with reactive wet strength resins (see chapter on wet strength) to achieve high wet strength levels, but such combinations are also powerful dry strength agents [e.g. Stratton 1989].

More recent research in this laboratory [Laine and Lindström 2001, Laine et al 2000, 2002a,b, 2003, a,b] and other laboratories [Mitikka-Eklund et al 1999, Watanabe et al 2004] has investigated a very different approach to the use of CMC, namely, the topochemical grafting of CMC onto cellulosic surfaces. CMC has no natural affinity for cellulosic fibres, because there is a strong electrostatic repulsion between the negatively charged cellulose surfaces and the CMC. It is, however, possible to deposit CMC onto cellulosic surfaces if the charge is screened by a suitable electrolyte. If they are simultaneously heated, CMC becomes irreversibly attached to the cellulosic surface, i.e. the surface has basically been grafted with CMC [Laine et al 2000]. Using such treatments considerable strength improvements can be obtained particularly for laboratory cooked, never-dried fibres as shown in Figure 22. On the basis of added amounts of the strength additive CMC shows a better strength improvement than cationic starch. The effect of 2% grafted CMC on the load-elongation curve is shown in Figure 22.

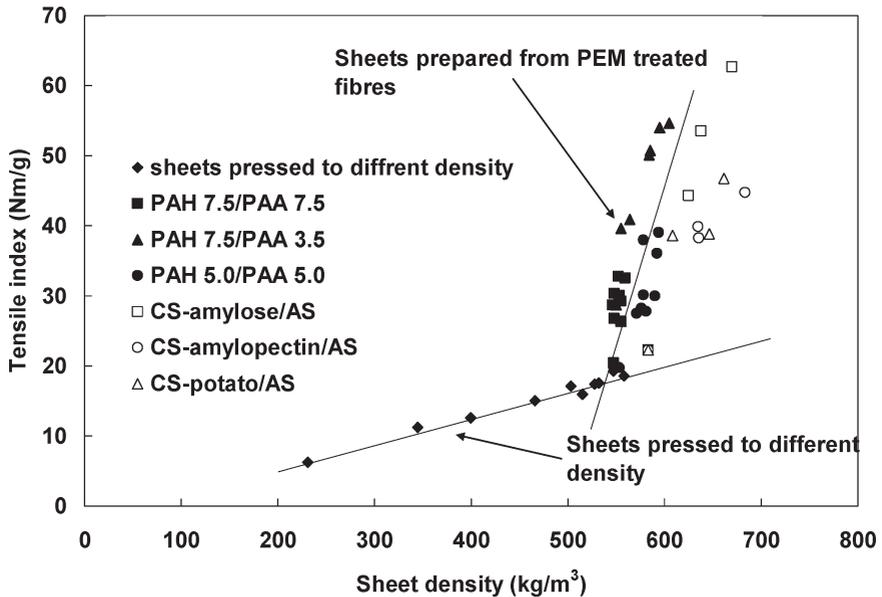
### *Application of polyelectrolyte multilayer (PEMs) to enhance paper strength*

The concept of using polyelectrolyte multilayers (PEMs) for the specific surface engineering of materials has recently been introduced [Decher 1997]. The technique is based on the phenomenon that oppositely charged polyelectrolytes form multilayers on surfaces when the surfaces are consecutively treated with them. The technique has rapidly developed since its introduction, and can now be used to produce a wide variety of surface properties [Decher and Schlenoff 2002].

This technique has also been applied to paper [Wågberg et al 2002], and it has been found that applying multilayers of polyallylamine (PAH) and polyacrylic acid (PAA) can more than double the strength of papers made of unbeaten bleached kraft fibres. Later research [Eriksson et al 2005, a–c] demonstrated that different properties could be produced with the use of different additives, and that the differences in properties could be traced back both to the physical structure of the multilayers and the chemistry of the polymers in



**Figure 22** a) Load elongation curve of comm. BSK vs elongation (2% grafted CMC) [Adapted from investigations reported by Laine et al 2002a]. b) Tensile index of bleached softwood kraft (BSK) pulps vs added amount of strength additive. (◆). Never-dried laboratory cooked BSK and CMC [Laine et al 2003b]. (■). Dried commercial BSK and CMC [Laine et al 2002a]. (▲). Dried commercial BSK and C-Starch [Lindström unpublished].



**Figure 23** Tensile index as function of density for untreated, wet-pressed sheets compared with all sheets made of PEM-treated fibres. All sheets were made of unbeaten, bleached softwood kraft pulp [Eriksson 2004]. PAH = polyallylamine, PAA = polyacrylic acid, CS-amylose = cationic starch with a high amylose content, CS-amylopectin = cationic starch with a high amylopectin content, CS-potato=cationic potato starch and AS = anionic potato starch.

them. A summary of some of these results is shown in Figure 23, in which the tensile strength of papers made from PEM-treated, unbeaten, bleached kraft fibres is shown as a function of sheet density. As shown in the Figure, this strength improvement can be achieved without any appreciable increase in sheet density [Eriksson 2004].

### Miscellaneous developments

There has recently been interest in the use of polyamines, such as polyvinylamines [Pelton and Hong 2002] and polyallylamines [Rathi and Bierman 2000], as dry strength additives. These resins, together with polyethyleneimine, also function as wet-strengthening agents (see wet strength below). Rathi and Bierman (2000) found very significant dry strength improvements when polyamines were used with a bleached kraft pulp, but less improvement when used with thermomechanical pulp.

Cationic styrene maleimide copolymers have also been investigated recently for use as wet and dry strength additives [Valton et al 2004].

Interestingly, the cellulose-binding domain can be used as a dry strengthening agent: Levy and Paldi (2003) fused two cellulose-binding domains to form a recombinant bifunctional protein, which acted as an efficient dry strengthening agent.

## **WET/MOIST STRENGTHENING OF PAPER**

### **General considerations**

During World War II, the need for wet strength papers initiated the development of wet strength resins. In Europe, the first wet strength paper was produced in Germany in 1939 by adding polyethyleneimine (PEI) to the pulp. Subsequently, intensive work led to the development of wet strength resins based on formaldehyde. The formaldehyde resins are more effective and cheaper than PEI is. In the 1960s, alkaline curing wet strength resins were developed and came to replace the formaldehyde resins.

The literature on this subject is extensive, and several good reviews are available [e.g. Bates et al 1999; Britt 1981; Chan 1994; Dunlop-Jones 1991; Espy 1992, 1995; Stannet 1967; Westfeldt 1979].

Apart from specialty papers (e.g. map paper and banknote paper), the main types of paper that contain wet strengthening agents are tissue and towelling papers and wet strengthened kraft and packaging papers. Chan (1994) has suggested that if paper retains more than 15% of its dry tensile strength, it can be considered to have wet strength properties; efficient wet strength resins may yield wet: dry strength ratios up to 50%.

It is generally agreed that covalent bonds are required for the wet strengthening of paper, although it has been questioned whether such agents as PEI could form covalent bonds (Schiff's base reaction) with cellulosic fibres. It has long been recognised that all wet strengthening agents also are efficient dry strength agents.

Over the years, there have been significant efforts to alleviate creep compression using various crosslinking agents. Much recent effort has been devoted to this issue and to producing wet strengthening agents that have an improved environmental profile. This review will focus on the former aspect and on the various chemistries employed. Therefore, an account will be made of the compressive properties of paper and of mechanosorptive creep.

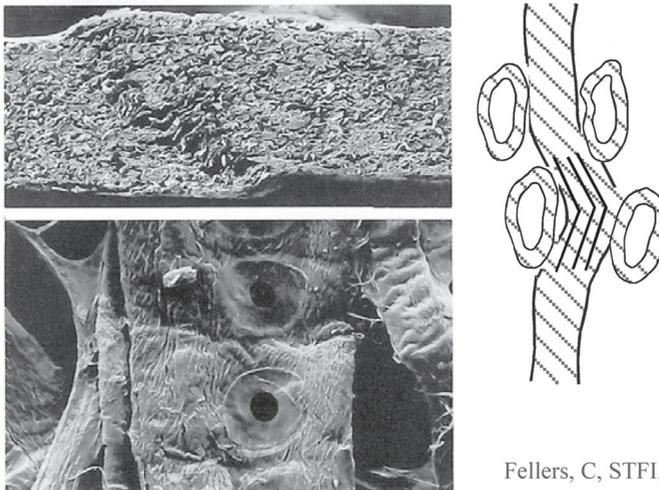
Several distinct lines of research over the past decade may be relevant to the subject. First, in the area of textile fibres, there have been extensive efforts to replace formaldehyde-containing resins in order to impart crosslinks for

the thermal creasing of wrinkle-resistant cotton fabrics. Multifunctional carboxylic acids have been explored for the purpose and this literature will be reviewed. Second, there has been extensive investigation of the TEMPO oxidation of cellulose, whereby aldehyde functionalities can be introduced onto cellulosic surfaces or carbohydrates.

### **Compression failure of paper**

It is difficult to find a unified view of the mechanism underlying compression failure in additive-free raw materials used for packaging products. Fellers and Donner (2001) have done an extensive review of the possible mechanisms, and with reference to general papers concerning composite materials, and have suggested that the following mechanisms – either singly or in combination – may be responsible for compressive failure in paper:

- I) Micro buckling of the fibres, matrix still elastic
- II) Matrix yielding followed by micro buckling of the fibres
- III) Debonding and interlaminar shear followed by microbuckling of the fibres
- IV) Shear failure (kink, shear band formation)
- V) Separation by transverse tension through the thickness (i.e. delamination)



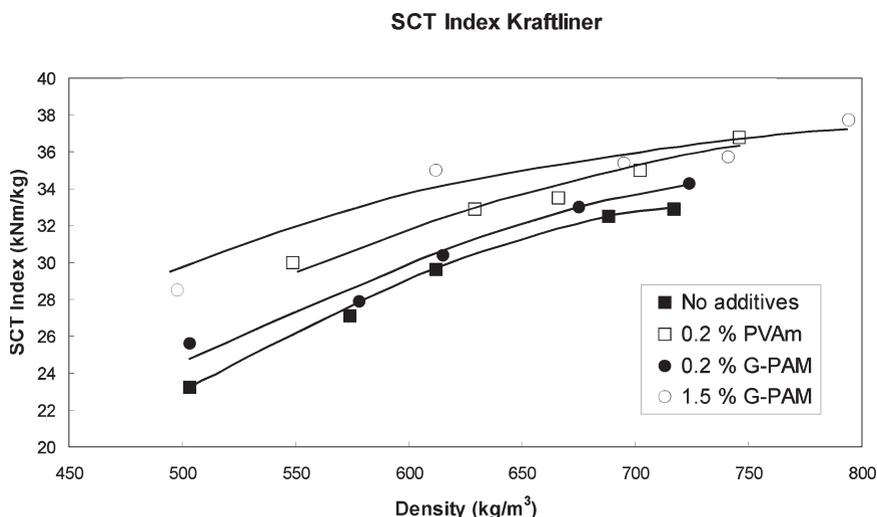
Fellers, C, STFI, Stockholm, Sweden

**Figure 24** Delamination zone of paper that has failed under compressive load. An obvious kink band is formed, but the exact mechanism underlying the failure is not known.

When examining the compression failure zone in paper, the situation depicted in Figure 24 is usually what is found. In this figure it can be seen that there is a kink band formation where the paper structure has been delaminated, but it is impossible to determine whether this is caused by fibre wall damage or buckling of the segments occurring before fibre wall delamination.

It is obvious from this figure that enhancing the bonding/sheet consolidation may greatly affect the compression strength of paper. Compression strength increases with the addition of wet strength resins, even at high sheet densities [Smith 1992]. It is believed that compression strength is limited by fibre–fibre bond strength at low sheet densities, but by fibre stiffness at high densities. Crosslinking presumably prevents cell wall delamination. Water sorption also has a strong impact on compression strength [Fellers and Bränge 1985].

Indeed, the possible changeover between the various mechanisms can also be seen in Figure 25, in which the compression strength of a paper made from a kraft liner pulp is shown as a function of paper density, with or without the addition of various additives. At low densities the additives have a great influence, but at higher densities the various papers depicted in Figure 25 tend



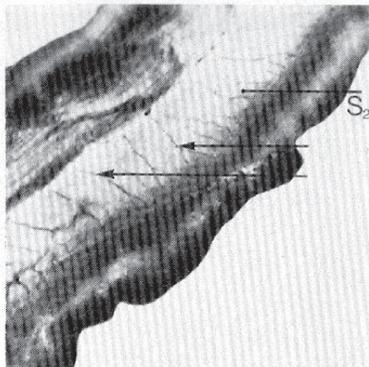
**Figure 25** Short-span Compression Strength of papers made from a kraft liner pulp with or without the addition of various additives: PVAm is polyvinylamine and G-PAM is glyoxal-treated polyacrylamide. As the density increases, the relative influence of the additives decreases [Wågberg, unpublished results].

to approach the same SCT (Shortspan Compression Strength) value. It might be that the strength of the joint between the fibres has great influence on paper strength at lower densities, whereas inherent fibre properties start to dominate at higher densities.

Paper treatments combining wet strength resins, wet pressing, and heat treatment can also considerably improve moist compression strength [Morgan 1997].

Sachs and Kuster (1981) linked the load deformation curve in compression to the behaviour of cross-sections of paper observed in a special device mounted inside a scanning electron microscope. They concluded that “the failure mechanism appears to involve the formation of dislocations in the form of protuberances from and fissures in the cell walls, detaching of fibre wall tissue, and separation of microfibrillar bonds (particularly of the  $S_1/S_2$ )”. These findings lead the authors to conclude that it is this separation of  $S_1$  and  $S_2$  that leads to the delamination of the fibre wall, and to the subsequent compressive failure of the linerboard. A typical micrograph from their research is shown in Figure 26, in which the fissures in the wall of fibres in the compressive failure zone are obvious.

On the other hand, Perkins et al (1981) has claimed, supported by a theoretical approach and experimental investigations, that compressive failure is a localised buckling phenomena and that the incremental transverse shear modulus is the most important variable for the compressive strength of



Kink band formation formed by cracks/delamination in the fibre wall

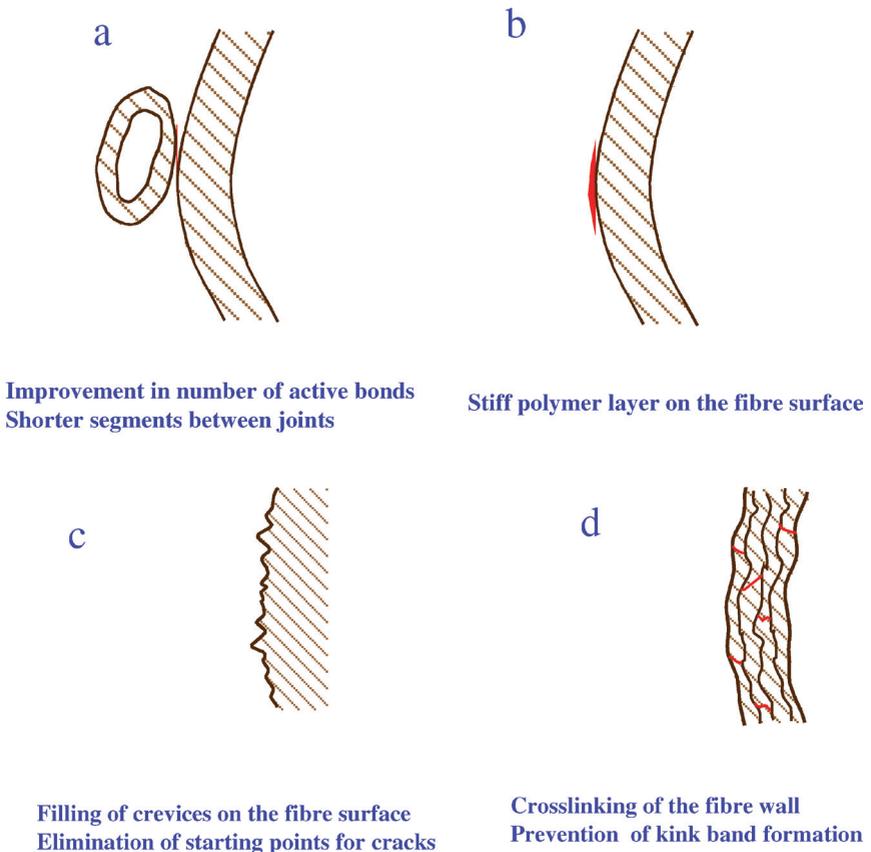
**Figure 26** Scanning electron micrograph of a fibre that has failed under compressive load. Fissures in the fibre wall were taken as an indication that it was fibre wall delamination that was the initial process underlying the compressive failure of the paper [Sachs and Kuster 1980].

linerboard. This theory is, however, difficult to apply since some of the parameters in the equations are virtually impossible to determine. Uesaka and Perkins (1983) have also suggested that compressive failure represents a bending and shear buckling phenomenon. The support for this conclusion included experiments that found a relationship between the interlaminar shear modulus and compressive strength. However, it should be mentioned that Uesaka and Perkins (1983) used a buckling equation that disregards transverse shear, and obtained a finite value for the critical load when the slenderness ratio approached zero. However, more rigorous analysis, taking account of transverse shear, shows that the critical load goes to infinity when the slenderness ratio approaches zero.

As is obvious from this short summary, there is no clear, single mechanism explaining compression failure in packaging papers. On the contrary, the authors feel it has been demonstrated that there might be several explanations, depending on the papermaking conditions, additives, and raw materials.

Dry strength additives might affect several fibre properties that could greatly influence the paper strength. First of all, such additives can increase the number of active joints in the paper. This decreases the average length of the free segments between fibre joints, and naturally this increases the buckling resistance of the paper. Second, additives might form a thin, very stiff layer on the fibre surfaces that could increase the buckling resistance of the fibre segment between two fibre–fibre joints. A third possibility is that the additives might block crevices and inhomogeneities in the fibre wall, and in this way remove possible initiation points for cracks that could propagate throughout the fibre wall under compressive loads. Finally, additives might crosslink the entire fibre wall, preventing delamination of the fibre wall when the paper is subjected to compressive loading. All these mechanisms are schematically shown in Figure 27. If it were possible to tailor chemicals so they could handle a single mechanism (of those mentioned in Figure 27), it should also be possible to determine the relative influence of the various mechanisms causing compressive failure in a paper under compression load.

The reason for summarising the possible mechanisms for compression failure of packaging papers is to draw the attention to the possibilities for improvements using the appropriate chemistry. Astonishingly little work has been done to investigate whether it is possible to improve the compression strength of paper through fibre wall strengthening, improved the bending stiffness of fibre segments, and increased joint strength between the fibres.



**Figure 27** Possible mechanisms by which additives improve the compression strength of paper following addition of dry strength additives. a) Increase in the number of active joints and hence a decrease in the efficient segment length between two joints. b) Formation of a stiff polymer layer on the fibre surface that might improve the buckling load of a single segment. c) Blocking of crevices and inhomogeneities that might be initiation points for cracks. d) Crosslinking of the fibre wall to prevent fibre wall delamination.

### Creep phenomena in paper materials

The mechanisms of creep (free volume theories, anisotropic swelling, and change in fibril angle) have recently been reviewed [Haslach 1994; Haslach

2000, 2002]. It is common to distinguish between moisture-accelerated and mechanosorptive creep (i.e. creep of paper accelerated in a variable relative humidity environment). It was found early on that paper creep accelerated significantly when paper was subjected to variable humidity levels. Byrd (1972a,b) suggested that creep was initiated by bond rupture. The area of mechanosorptive creep has recently been reviewed by Alfthan (2004), and the reader is referred to this and previously cited references for a more detailed account of creep phenomena.

The time-dependent mechanical behaviour of paper is significantly affected by the moisture content of the paper and less so by the temperature. It has long been known that moisture sorption per se is difficult to affect by crosslinking reactions, unless the fibres are extensively derivatised [see e.g. Stannet 1967]. Moisture sorption is primarily affected by the chemical composition of the fibres and their supramolecular structure.

A key issue is whether the rate-dependent response under a tensile load prior to fracture is caused by structural changes within the individual fibres or by mechanisms involving inter-fibre bonds. Brezinsky (1956) argued from creep tests that deformation of paper sheets depends entirely on molecular phenomena, because the nearly ideal creep curves obtained could not be produced if creep were due to macroscopic fibre changes such as the uncurling, straightening, and relative slippage of fibres, or due to bond breaking. The Brezinsky data were corroborated by Schulz (1961), who found that sheets treated with wet straining creep less than similar though untreated sheets. Schultz hypothesised that wet straining causes a more uniform distribution of stress in the dry sheet, by aligning fibres so that they carry more load; this would increase strength and reduce creep. It was, however, later found [Parker 1962] that wet pressing improved bond strength and reduced creep, so it was concluded that both inter-fibre and intra-fibre mechanisms contributed to creep. Further evidence that stress-induced deformation involves the inter-fibre bonds is given by optical and porosity tests showing that there is an increase in porosity and light scattering during creep [Sanborn 1962].

From these investigations, it is likely that both cell wall crosslinking and inter-fibre crosslinking can be expected to make a positive contribution to reducing creep.

Regarding mechano-sorptive creep, the mechanism is usually interpreted in terms of residual or induced stress concentrations in the sheet at various structural levels [Alfthan 2004]. Indeed, Habeger, and Coffins (2000, 2001) were able to show that a very simple rheological model can exhibit accelerated creep if the model includes variations in the hygroexpansion. Stress concentrations may occur at various structural levels, such as in fibre crossings (microcompressions), as drying history-dependent variations in the free

volume of cellulose, or in the  $z$  direction of the sheet induced by drying. It is not yet possible to pinpoint whether stress concentrations at one level are more important than at others. It is obvious, however, that it is more difficult to speculate as to the role of crosslinking agents in the context of residual stresses in paper sheets.

## BASIC WORKING MECHANISMS OF WET STRENGTH RESINS

The general working mechanisms of common wet strength agents have been extensively studied, and the overall situation as discussed below can be extracted from review texts. In this context, aspects important for paper creep are also discussed. However, no literature treats the effects of commercial wet strength resins on paper creep, so the discussion will be made using indirect analysis.

Commercial resins may be divided into the following major groups:

- Urea-formaldehyde and melamine resins
- Alkaline curing polymeric amine-epichlorohydrine resins
- Glyoxalated polyacrylamide resins

Apart from these resins, a number of other chemicals have been tried out for the wet stiffening of board, and these will be covered under a separate heading below.

There are *two principal mechanisms* for the development of wet strength.

**1) Protection mechanism.** – After adsorption and possible penetration into the cell wall of fibres (depending on contact time and the  $M_w$  of the resin), the resin will homo-crosslink itself. Two separate cases may be conceived:

- A. The resin is of high  $M_w$  and will homo-crosslink on the surface of fibres, which may prevent the swelling of fibres in contact with water.
- B. The resin penetrates the cell wall, where it will homo-crosslink and form an interpenetrating network with the cell wall of fibres.

Protection mechanism A is not expected to produce any sizeable protection against creep under moist conditions, as the moisture sorption will not be significantly affected; swelling reduction will only occur where the fibre is in direct contact with water. However, protection mechanism B is expected to have a significant effect, reducing creep under moist conditions.

**2) Reinforcement mechanism.** – The resin reacts with cellulose (or other wood components) to form covalent bonds in the cell wall of fibres or in the inter-fibre bonding region. Again, two cases may be distinguished:

- A. The resin is of high  $M_w$  and will hetero-crosslink on the surface of fibres, which may create inter-fibre covalent bonds.
- B. The resin penetrates the cell wall, where it will hetero-crosslink and form a densely crosslinked cellulose network.

Reinforcement mechanism A is expected to reduce creep in low sheet density structures, in which inter-fibre bonding plays a role in creep. Reinforcement mechanism B is expected to have a very significant effect on reducing creep in sheets in which creep is dominated by the rheology of the fibre cell wall itself. It is also expected that such treatments will have a very significant effect on the embrittlement of the paper structure.

It has long been recognised that reinforcement mechanism A is the most important in producing good wet strength of paper. It has, for instance, been known that the migration of cationic polymers from the surface of fibres to their interiors diminishes the effectiveness of the additive (e.g. Espy 1995). This mechanism is expected to have a positive effect on the creep properties of paper.

It should be stated in this context, that few experimental studies have actually attempted to determine the wet strengthening mechanism [see e.g. Hazard et al 1961; Mayhood et al 1961; Russel et al 1964], and all these were carried out many years ago. The effects of melamine formaldehyde (MF) and PAE resins on the in-plane tensile properties of paper and fibres were investigated, as were the shear resistance of inter-fibre contacts [Mayhood et al 1961] and the degree of inter-fibre bonding. Resins do not affect single-fibre properties, but rather *wet* properties. The wet shear strength increased with the use of MF and PAE, and the contact area remained unaffected when the bonded area was wet strengthened. For surface crosslinked fibres it has been suggested that the shear strength of the cell wall limits the ultimate wet strength of paper [Taylor 1968]. This behaviour was interpreted as a protective action of the resin–fibre surface complex, analogous to polyelectrolyte complexes (PECs) [Russel et al 1964].

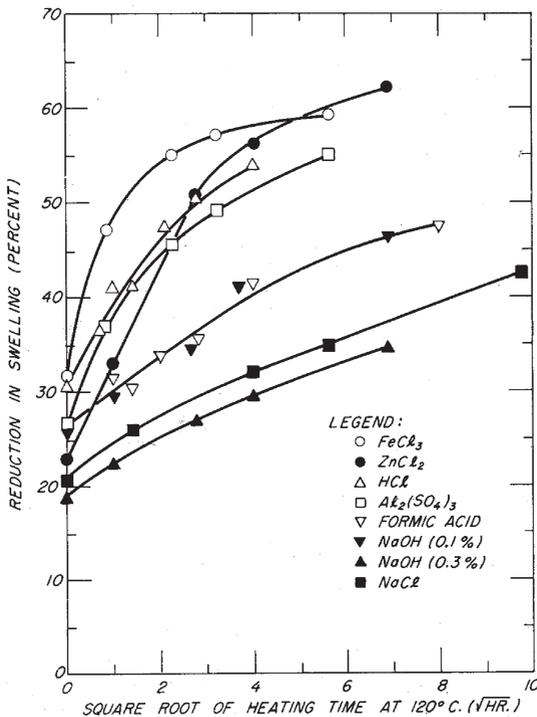
The overall situation described above seems to be generally accepted in the scientific community.

## WET STRENGTHENING TREATMENTS

### Early literature on catalysed heat treatment and crosslinking

There have been extensive efforts over the years to crosslink the cell wall to obtain wet paper stiffness. A brief review of these efforts provides a historical context for these efforts to decrease the sensitivity of paper materials to moist conditions.

It has long been known that formaldehyde (HCHO) is an efficient crosslinking agent for cellulose fibres [e.g. Stamm 1959]. Hence, paper can be dimensionally stabilised by means of formaldehyde (vapour) crosslinking. Wet compression strength was found to improve greatly with such treatments [Cohen et al 1959a,b]. A range of different crosslinking was investigated early on for the purpose of improving the wet stiffness of paper [e.g. Trout 1957; Ward and Morak 1968].



**Figure 28** Dependence of swelling reduction on the duration of heating at 120°C with catalyst present [Cohen et al 1959].

The presence of a catalyst (e.g.  $ZnCl_2$ ) is usually necessary. Heat treatment in the absence of HCHO but in the presence of a catalyst also imparts dimensional stability. Figure 28 shows how the swelling of paper is reduced in the presence of various catalysts. It was also recognised early on that crosslinking agents make paper brittle, see Figure 29. Aluminium sulphate was found to have a significant effect. Later investigations also revealed that the addition of precipitated aluminium hydroxide significantly improves the wet stiffness of paper [Michell et al 1983].

Heat treatments as a way to impart dimensional stability and wet strength were also later explored by Back and co-workers in a number of publications [Back and Klinga 1963; Back 1967a,b]. It was suggested that heat treatments resulted in thermal (“auto crosslinking”) crosslinking by the formation of ester, hemiacetal, or other types of crosslinks. High temperature treatment of linerboard as a technically viable process to impart wet stiffness of linerboard has been explored as well [Back and Stenberg 1976, 1977; Stenberg 1978]. These developments took place simultaneously with the development of press drying technology (see below).

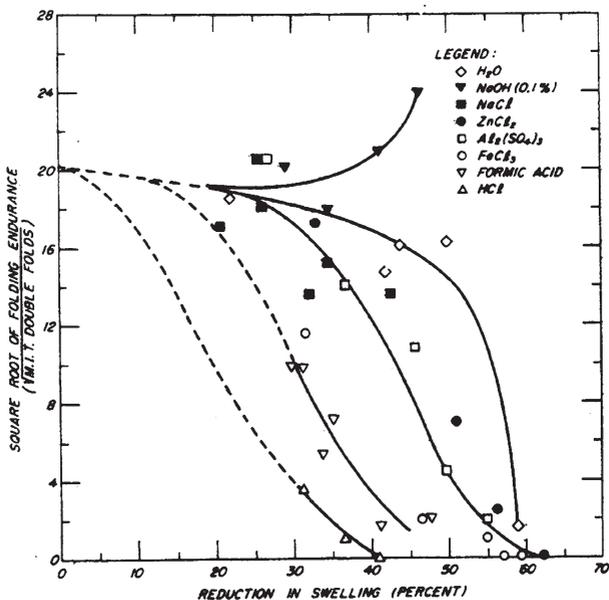


Figure 29 Decrease in folding endurance with increasing dimensional stability [Cohen et al 1959].

The mechanism of crosslinking cellulose fibres with HCHO was later investigated by Caulfield and Weatherwax (1976a). It was also found that the moisture content during crosslinking is critical [Caulfield and Weatherwax 1976b; Weatherwax and Caulfield 1978a]. Dry crosslinking with HCHO vapour was more efficient in creating short crosslinkages, which could resist water swelling. The technology of HCHO crosslinking was subsequently developed using SO<sub>2</sub> in combination with HCHO – SOFORM technology. It was believed that methylolsulphonic acid, the reaction product of HCHO and SO<sub>2</sub>, was the active crosslinking agent [Weatherwax and Caulfield 1978b].

It was recognised that wet stiffness required the crosslinking of the cell wall. It was speculated that the poor penetration of larger molecules, as in commercial wet strength resins, might account for the failure of some polymeric resins to impart good wet stiffness. This also explains the observation that wet strengthened paper fails by a shear mechanism within the cell wall of fibres [Mayhood et al 1961; Russell et al 1964].

## Chemistry of commercially important wet strengthening agents

### *Urea formaldehyde (UF) resins*

Urea reacts with formaldehyde under slightly alkaline conditions to form methylolurea. When the pH is lowered (the optimum pH is 4.5) a polymer is formed by the self-condensation of these methylol groups. This second stage is promoted by the low pH and a high temperature and will result in methylene or ether linkages with the elimination of water. Commercial resins are all cationic.

The activation energy associated with the development of wet strength strongly suggests that the wet strengthening mechanism is homo-crosslinking [Hazard et al 1961; Jurecic et al 1958; Stannett 1967]. There is also a consensus in the literature [Espy 1995; Chan 1994] that UF resins function exclusively by self-crosslinking.

As the wet strengthening mechanism of UF resins is classified as *protection*, it might be expected that UF resins would be of less interest than cellulose reactive resins in efforts to decrease creep in paper.

### *Melamine formaldehyde (MF) resins*

Melamine reacts with formaldehyde under slightly alkaline conditions to form a series of methylol melamines. Depending on the number of moles of formaldehyde present, a range of products from monomethylol to hexam-

ethylol melamine can be formed. Most commercial MF resins are of higher  $M_w$  and are made by condensing two or more monomer units, together with the elimination of water, under high temperature and low pH conditions. MF colloids acquire cationic charges due to the association of the amino nitrogen from methylol melamine with hydrochloric acid to give a water-soluble acid salt. A molar ratio of 3:1 between formaldehyde and melamine seems to produce the best MF colloid for wet strength applications.

Model experiments [Bates 1966] reveal that MF resins can react with cellulose, but as MF resins have chemical reaction chemistries similar to those of UF resins, it is generally assumed that homo-crosslinking is a major factor in the wet strengthening with MF resins (protective mechanism). This conclusion is mainly supported by the fact that the activation energy of hydrolytic cleavage is the same (23 kcal/mole) for both UF and MF resins [Chan 1994].

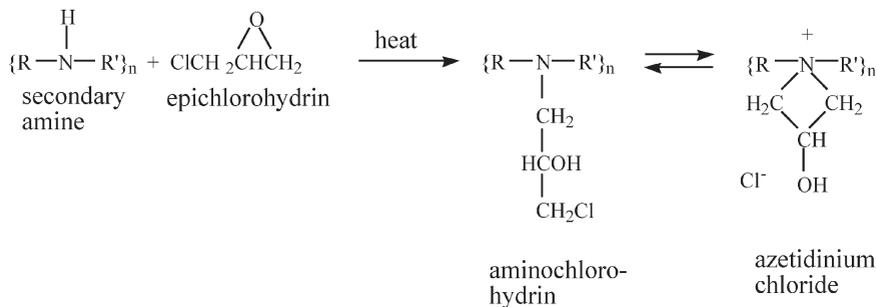
Thus MF resins are powerful wet strengthening agents, albeit limited to acidic use under slightly alkaline papermaking conditions. Indeed, MF resins are better than UF resins are at imparting moist stiffness to paper sheets [Fahey 1962].

#### *Alkaline curing polymeric amine-epichlorohydrine resins*

These wet strength resins are probably the most important commercial resins in this context, and their chemistry has thus been more thoroughly reviewed. The readers wishing more thorough literature reviews of these agents are referred to Chan (1994), Dunlop-Jones (1991), and Espy (1992, 1995). Some fairly recent publications also highlight some of the detailed chemistry [Devore and Fischer 1993; Espy and Terence 1988; Fischer 1996].

The first alkaline-curing wet strength resins to become commercially practical were the poly(aminoamide)-epichlorohydrin (PAE) resins. These resins rapidly replaced UF and MF resins in many applications. Later, polyalkylenepolyamine-epichlorohydrin (PAPAE) and amine polymer-epichlorohydrin (APE) were introduced commercially. These are, like PAE, cationic and thermosetting under near neutral and alkaline pH conditions. The terms PAE, PAPAE, and APE describe the backbone polymers of the resins. Therefore PAPAE and APE resins are sometimes categorised together as polyamine-epichlorohydrin resins [Chan 1994; Espy 1995]. The poly(aminoamide) backbone of a PAE resin is a result of the reaction between adipic acid and diethylenetriamine.

The resulting poly(aminoamide) is subsequently reacted with epichlorohydrin. In the PAPAE resin a polyalkylenepolyamine is reacted directly with epichlorohydrin, while in the APE resin an amine polymer is reacted with epichlorohydrin. The structure of the final wet strength resin depends on



**Figure 30** Reaction of epichlorohydrin and secondary amines.

whether the reaction partner of epichlorohydrin is a primary, secondary, or tertiary amine. Secondary amines react with epichlorohydrin to form tertiary aminochlorohydrins, which form cyclic structures of the 3-hydroxy-azetidinium salt type (see Figure 30). Since these structures are fairly constrained they are also fairly reactive.

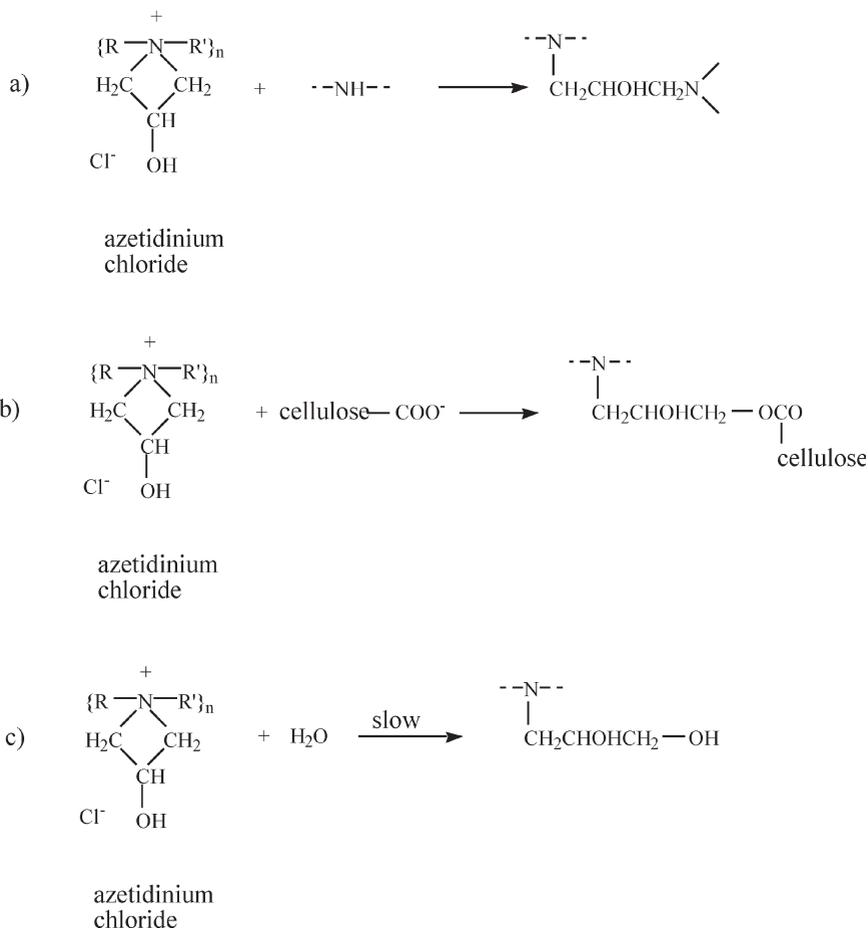
The most important PAE resins are derived from secondary amines and have the 3-hydroxy-azetidinium ring as their principal reactive group. Tertiary amines react with epichlorohydrin to form a glycidyl (2,3-epoxypropyl) ammonium salt. The functional groups can occur independently of the category of backbone polymer. The most important resins having 3-hydroxy-azetidinium as their reactive groups are of the PAE and PAPAE type, and the most important resins having glycidyl (2,3-epoxypropyl) ammonium as their reactive groups are of the PAE and APE type. On a weight basis, PAPAE resins are less effective than PAE resins, while many APE resins, especially of the epoxide type, are more effective. PAE is the most important alkaline curing wet strength resin. PAPAE and APE resins that were later introduced to the paper industry have not reached the same volume of use.

The 3-hydroxy-azetidinium ring confers both reactivity and a permanent (pH independent) cationic charge. The 3-hydroxy-azetidinium ring may react in three different manners:

- a) Reaction with other PAE macromolecules (homo-crosslinking)
- b) Reaction with cellulose fibres (hetero-crosslinking)
- c) Reaction with water

The three different reactions of the 3-hydroxy-azetidinium ring are shown in Figure 31.

Model compound studies using sucrose or methylglucoside indicate that PAE resins do not react with cellulose hydroxyl groups [Espy 1995]. In



**Figure 31a)–c)** Different reaction mechanisms of azetidinium chloride from PAE: reaction with secondary amines, cellulose carboxyl groups, and water.

contrast, direct and indirect evidence suggests that the 3-hydroxy-azetidinium groups react with the carboxylate groups of pulp [Espy 1995]. For instance, direct spectroscopic evidence for the reaction of 3-hydroxy-azetidinium groups with pulp carboxylate to form ester groups has been reported [Wågberg and Björklund 1993]. This latter aspect is particularly important in commercial applications, in which the carboxyl group content of the pulp has a very strong influence on both covalent bond formation and the wet strength

of the paper [Laine et al 2002]. Alternatively, carboxymethylcellulose (CMC) may be used as a papermaking adjuvant in conjunction with PAE resins to impart wet strength [Dunlop-Jones 1991; Chan 1994; Gernandt et al 2003].

To increase creep resistance under moist conditions it would thus be advantageous to oxidise or in other ways derivatise the cellulose, in order to increase the carboxyl group content of the cell wall of fibres. This is because cell wall crosslinking is thought to be advantageous for decreasing the creep rate under moist conditions.

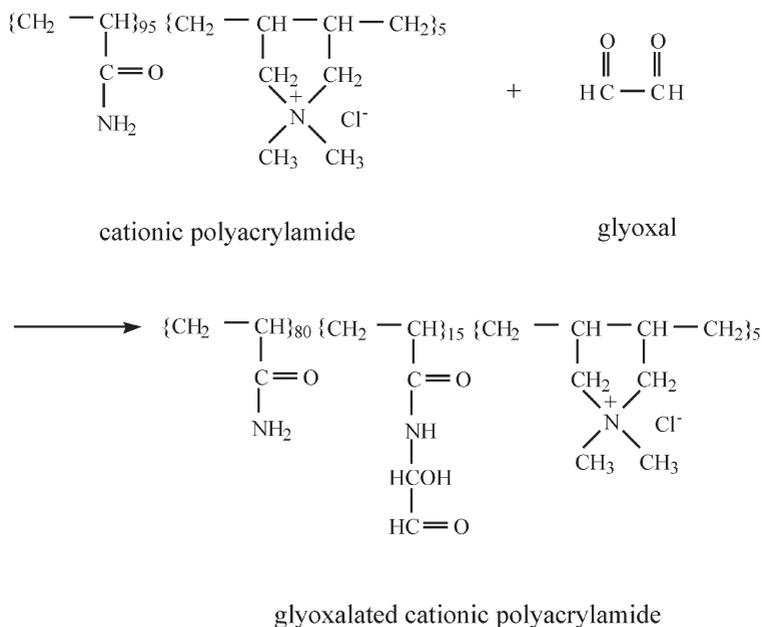
### *Glyoxalated polyacrylamide resins (G-PAM)*

It was recognised early on [Head 1958; Kyle and Ward 1968; Moyer and Stagg 1965; Frick and Harper 1982] that glyoxal was a crosslinking agent that was particularly efficient at imparting wet stiffness to unbleached linerboard under moist conditions. Glyoxal, as multifunctional aldehydes, enjoys the advantages of relatively low curing temperatures. Renewed investigations in this field have used glyoxal and glutaraldehyde as crosslinking agents [Xu et al 2001, 2002, 2004]. Catalysts are generally needed for glutaraldehyde, and this molecule is a very efficient crosslinking agent that has the added benefit of being less destructive than glyoxal in terms of making paper brittle.

In order to make aldehyde crosslinking compatible with wet-end additions, the glyoxalated polyacrylamide resins were developed and introduced in the 1960s.

These resins are classified as temporary wet strength resins and have primarily been used for tissue papers; recently, they have also been offered as efficient dry/wet strength agents for other grades of paper. In these resins, acrylamide is usually copolymerised with a cationic monomer, such as diallyldimethyl ammonium chloride, yielding a cationic polyacrylamide (C-PAM); after this, the C-PAM is reacted with glyoxal, yielding G-PAM as shown in Figure 32.

As can be seen in Figure 32, the final G-PAM resin contains three active groups: unreacted amines, amides reacted with glyoxal, and quaternary ammonium cations. The unreacted amines are free to form hydrogen bonds with the hydroxyl groups on the cellulose, resulting in increased dry strength. The quaternary ammonium cations are important for interaction with negatively charged fibres. The amides reacted with glyoxal are the groups that will form both homo and hetero crosslinks. Obviously, in preparing G-PAM, the amount of glyoxal used can control the reactivity of the final resin. Evidence [Chan 1994; Dunlop-Jones 1991] strongly suggests that G-PAM imparts wet strength to paper primarily through the formation of covalent bonds

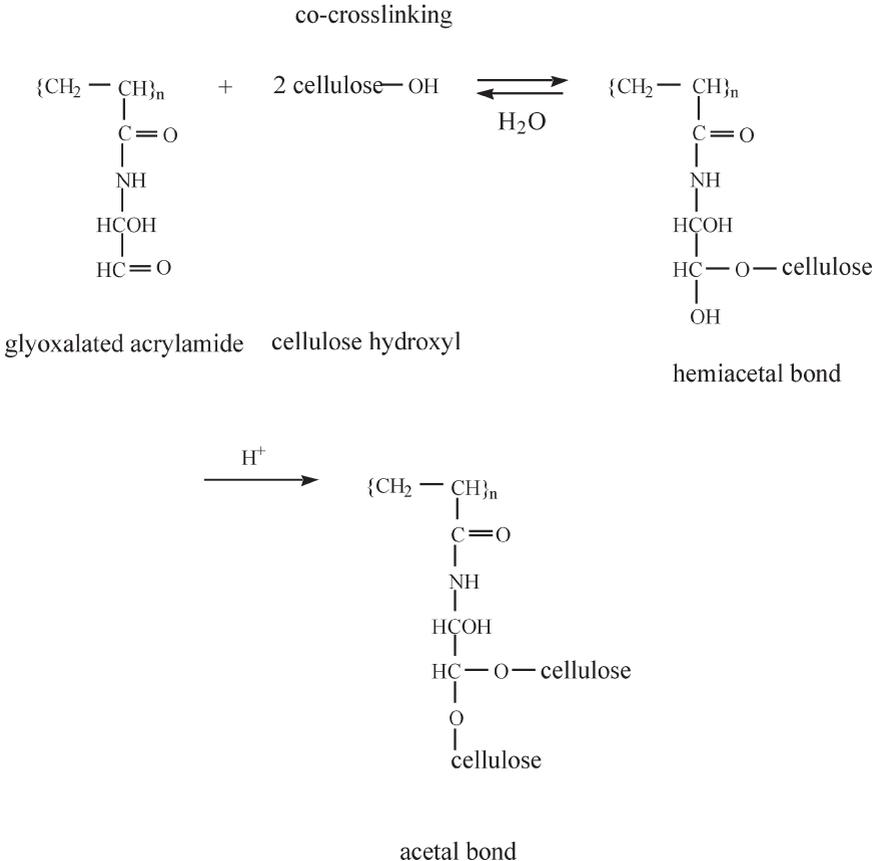


**Figure 32** Glyoxalated cationic polyacrylamide.

(hemiacetal and acetal) between the free aldehydes on its reactive group and the hydroxyl groups on fibres (see Figure 33).

Homo-crosslinks can also be formed between aldehydes and free amines.

G-PAMs have usually been employed in making tissue products, in the neutral to alkaline region, but G-PAMs are more reactive towards cellulose in the acidic region. Hence, G-PAMs are truly reactive resins that might have the potential to reduce creep in paper products. Still, G-PAMs are classified as temporary wet strength resins, and the critical issue is whether hydrolysis takes place under wet but not under moist conditions. G-PAMs have not yet been explored for their potential to impart wet stiffness. However, in view of the earlier mentioned experiments with the use of glyoxal to impart moist stiffness to linerboard, it might be expected that G-PAMs could also be used to reduce moist creep.



**Figure 33** Co-crosslinking reactions between the active group on G-PAM and hydroxyl groups on cellulose. Either hemiacetal or acetal bonds may be formed, depending on the pH.

### Miscellaneous treatments. Wet strenghtening/crosslinking

#### *Use of oxidised polysaccharides*

Since the initial discovery in 1959 that dialdehyde starch (DAS) was an efficient wet strength agent, there have been various approaches to oxidising either the cellulosic fibres or polysaccharides, and using them as a papermaking adjuvant. DAS can easily be prepared by means of the periodic acid oxidation of starch [Hamerstrand et al 1963; Borchert and Mirza 1964,

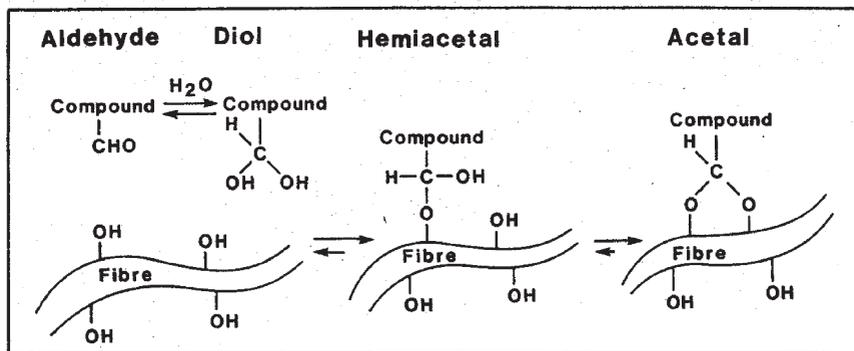


Figure 34 Conversion of aldehyde groups to diol and the formation of hemiacetal and acetal bonds between the aldehyde and hydroxyl groups.

Hofreiter 1965]. The use of DAS was even commercialised in Japan, though the process was later abandoned for safety reasons. The use of periodate oxidised galactomannans as wet and dry strength agents have also been reported [Opie and Keen 1964].

The principal way to produce wet strengthening using aldehydes is illustrated in Figure 34. The aldehyde basically isomerises to its diol, which then reacts with cellulose hydroxyl groups in one (yielding a hemiacetal) or in two steps (yielding an acetal).

One major difficulty with the use of aldehyde functional polymers is their tendency to undergo crosslinking and oxidation. To overcome this problem, acetal-containing starches [Solarek et al 1987, 1988; Laleg et al 1991; Laleg and Pikulik 1991, 1993a, b] can be manufactured by reacting the starch with an acetal, for example, N-(2,2-dimethoxyethyl)-N-methyl-2-chloroacetamide (see Figure 35). It can then be hydrolysed to its corresponding aldehyde and

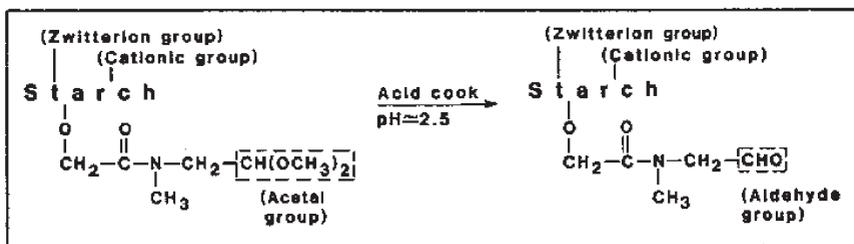


Figure 35 Conversion of the acetal group on starch to an aldehyde.

used as a wet strengthening agent. Such wet strengthening agents have found commercial application in the tissue sector.

Another approach is to use polyacrylamide acetal [Jansma et al 1995]. Model experiments using a dextran diethyl acetal have also reported that this substance can produce wet strength [Chen et al 2002].

It is also possible to oxidise polysaccharides using oxidative enzymes. Galactoseoxidase can, for instance, oxidise guar galactomannan, yielding useful materials for wet strengthening purposes [Hartmans et al 2003].

### *TEMPO oxidation of carbohydrates*

The oxidation of cellulose and carbohydrates in general offers a route to introduce reactive groups onto cellulose, which could be used in wet strengthening applications. Dialdehyde starch (see above) has, for instance, been used as a wet strengthening agent on a commercial basis. Cellulose oxidation has been the subject of numerous studies over the years, and interest in the field has revived since TEMPO-mediated oxidation methods have been developed. In recent years, this technique has been extensively used for the oxidation of many different carbohydrates. This may be an important application area, judging from the patent activities in the field.

TEMPO oxidation refers to catalytic oxidation of carbohydrates using the stable nitroxyl radical, 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO). A simplified scheme is given in Figure 36.

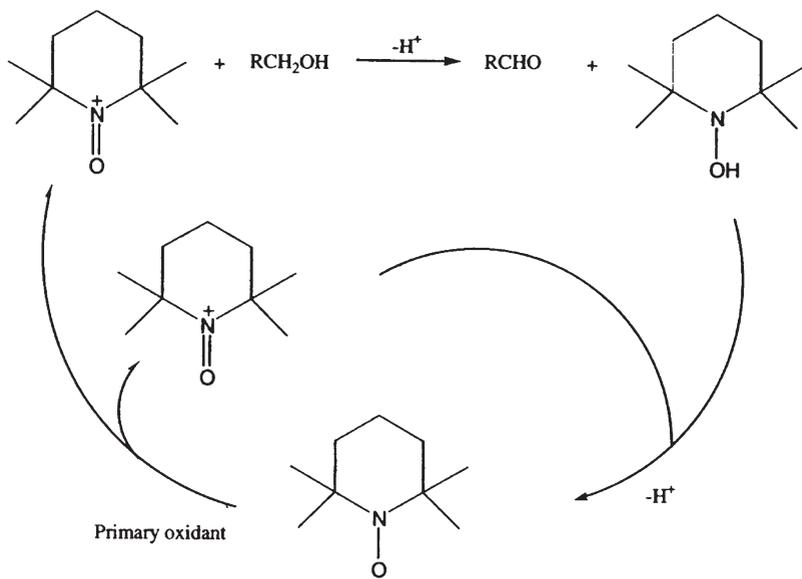
The oxidation is often stoichiometric and selective (C-6), and to minimise the use of TEMPO, the nitrosonium ion is continuously regenerated *in situ*, using a primary oxidant such as sodium hypochlorite or an oxidative enzyme such as laccase [Viikari et al 1999].

The literature dealing with TEMPO has recently been reviewed by Bragd et al (2004).

The first oxidation of monosaccharides by TEMPO oxidation was reported by Davis and Flitsch (1993). An early review of the TEMPO oxidation of non-carbohydrate nitrosonium oxidations is also available [Bobbitt and Flores 1988]. Several examples of the selective oxidation of polysaccharides were subsequently reported by de Nooy and Besemer (1995), de Nooy et al (1995); Chang and Robyt (1996).

A decided advantage is that this type of oxidation is conducted under aqueous conditions. The oxidation is limited when applied to insoluble native cellulosic fibres [Kitaoka et al 1999], but the surface of the fibres may be oxidised.

Patent activities have been extensive in recent years, and many patents and patent applications have been filed for the TEMPO oxidation of poly-



**Figure 36** A simplified mechanism for the catalytic cycle in the TEMPO-mediated oxidation of alcohol substrates under weakly alkaline conditions. The TEMPO radical is continuously regenerated in situ by reaction of the nitronium ion and hydroxylamine.

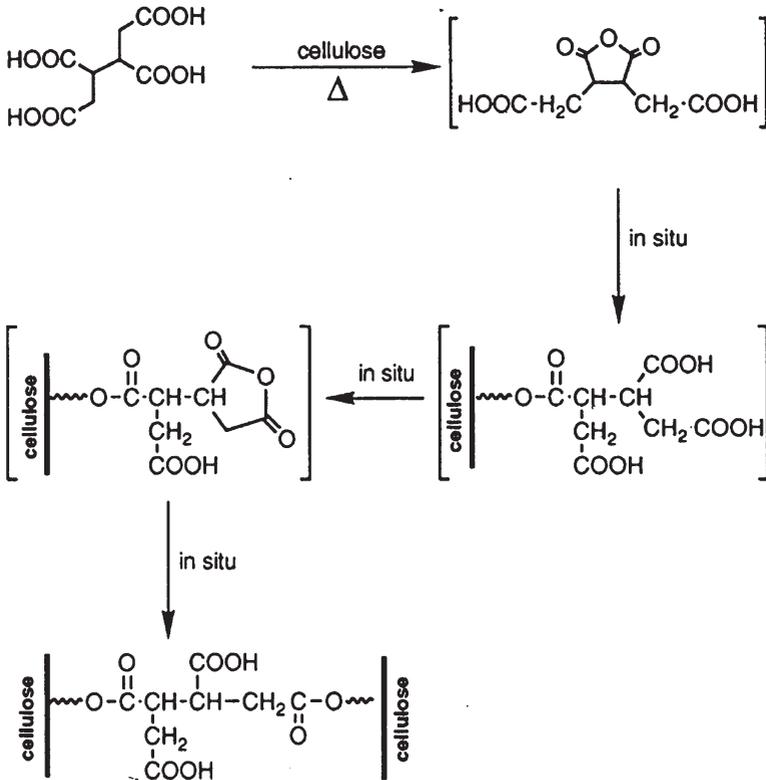
saccharides [see e.g. Brady et al 2002; Bragd et al 2003; Cimecioglu et al 2002, 2004; Cimecioglu and Harkins 2001, 2002, 2003; Cimecioglu and Thomaides 2003; Besemer and De Nooy 1995; Besemer et al 1999, 2000, 2003; Jaschinski 2002; Jaschinski et al 2000, 2003; Jetten et al 2004; Komen et al 2003; Thornton et al 2003; Weerawarna et al 2003]. The aim is to oxidise the C-6 of the polysaccharide to an aldehyde and gain wet strength. None of these applications have yet found commercial application.

*Oxidation of polysaccharides containing cis-OH groups to their corresponding aldehydes*

It has long been known that polysaccharides containing cis-configured hydroxyl groups, such as mannan and galactose, can readily be oxidised with ozone to yield their corresponding aldehyde groups by means of chain cleavage [Angibeaud et al 1985]. It has also been discovered that paper products containing oxidised fibres or oxidised gums (e.g. guar and karaya) acquire a temporary wet strength [Smith 1997a,b, 1998; Smith and Headlam 1997a,b, 2001].

*Cross-linking of cellulose using polycarboxylic acids*

N-methylol reagents, such as dimethylol dihydroxyethyleneurea (DMDHEU), have traditionally been used in the textile industry as crosslinking agents for cotton cellulose, to produce wrinkle-resistant cotton fabrics. Since the identification of formaldehyde as a probable human carcinogen, extensive efforts have been made to use polycarboxylic acids as durable press finishing agents to replace DMDHEU [e.g. Kottes et al 1989; Laemmermann 1992; Welch 1988; Welch and Andrews 1989, 1990]. Typical polycarboxylic acids studied are succinic acid (SA), citric acid (CA), tricarballic acid (TCA), and 1,2,3,4-butaneteracarboxylic acid (BTCA). These molecules crosslink



**Figure 37** Mechanism of the thermal crosslinking of cellulose with BTCA [Zhou et al 1993].

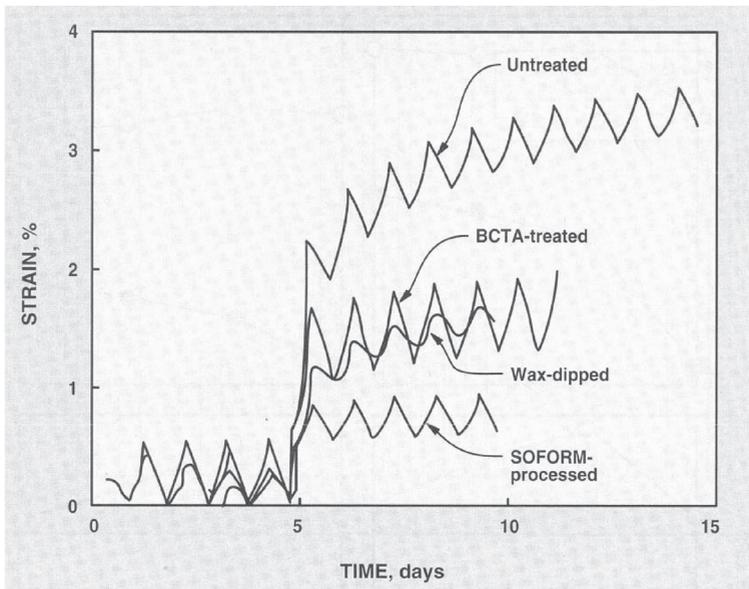
cellulose by means of esterification. Ester crosslinking of cotton has a long history and was first documented in the 1960s [Gagliardi and Shippee 1962; Rowland et al 1967; Rowland and Brannan 1968]. The reaction between cellulose and these carboxylic acids has been investigated, and it was found that all the effective polycarboxylic acids contain three or more carboxyl groups [e.g. Rowland et al 1967; Kottes et al 1989]. It was also recognised early on that polyacrylic acid (PAA) could produce efficient wet strengthening if paper treated with it was cured at high temperatures [Neogi and Jensen 1980]. Subsequently, it was found that the esterification reaction goes over a five-member cyclic anhydride intermediate, and that those polycarboxylic acids that readily form such cyclic intermediates are the most effective crosslinking agents [Yang 1993; Yang and Wang 1996 a,b, 1997]. The chemistry is outlined, using BTCA as an example, in Figure 37.

The reaction is catalysed by a number of additives, but the most effective catalyst has been found to be sodium hypophosphite [Welch 1988; Welch and Andrews 1990].

Following these investigations in the textile field, there was interest in improving the wet strength and dimensional stability of paper by using these same chemistries. These studies have been compiled in Table 3.

**Table 3** Recent paper wet strengthening studies using various polycarboxylic acids: succinic acid (SA), maleic acid (MA), citric acid (CA), tricarballic acid (TCA), butanetetracarboxylic acid (BTCA), polymaleic acid (PMA), terpolymer of maleic acid, acrylic acid, and vinylalcohol (TPMA), poly(methyl vinyl ether-co-maleic acid (PMMA), and polyethylene maleic anhydride (PEMA)

SA	MA	CA	TCA	BTCA	PAA	PMA	TPMA	PMMA	PEMA	Reference
x	x	x	x	x						Zhou et al 1993
		x		x						Caulfield 1994
x	x	x		x						Horie and Biermann 1994
x			x	x						Zhou et al 1995
				x		x				Yang et al 1996
				x		x	x			Xu et al 1998
				x		x				Yang and Xu 1998
						x		x		Xu et al 1999
				x					x	Xu and Yang 1999
						x				Xu et al 2001



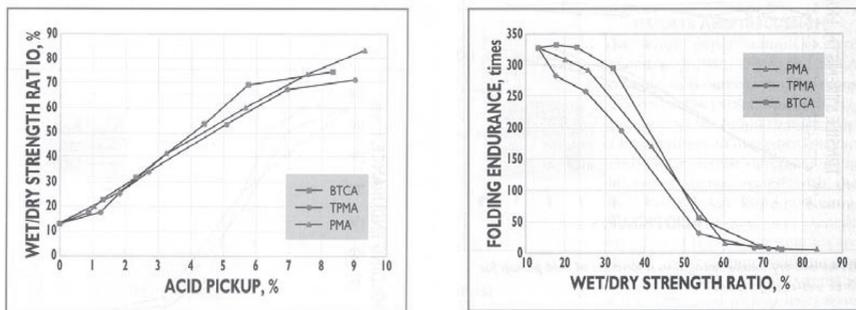
**Figure 38** Effect of BTCA crosslinking on the long-term creep of paperboard loaded in tension and exposed to daily cyclic humidity environment (30–90% RH) [Caulfield 1994].

The first such studies on paper [Zhou et al 1993] confirmed that BTCA was a superior crosslinking agent compared to SA, MA, CA, and TCA. BTCA use produced very high wet: dry strength ratios (over 0.6), and greatly improved the dimensional stability. Long-term creep properties, when exposed to a cyclic humidity environment, were significantly improved by BTCA crosslinking (see Figure 38).

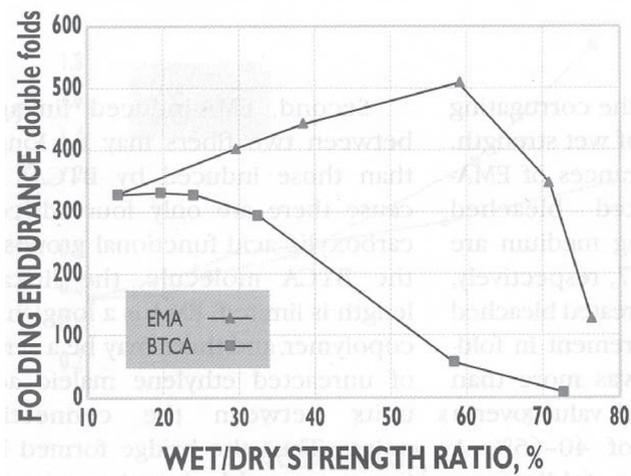
It was clearly recognised in these early investigations that BTCA crosslinking also was associated with a considerable embrittlement of the paper.

Subsequently, it was found [Yang et al 1996; Xu et al 1998] that polymaleic acid (PMA) was found to be equally effective as BTCA as illustrated in Figure 39.

Later investigations have also focused on measures to escape from the wet strength–brittleness relationship. It was found that small molecular size molecules, able to crosslink the cell wall of fibres, were more detrimental to fracture resistance than were larger crosslinking molecules, which primarily crosslink in the inter-fibre regions [Xu and Yang 1999]. Other polycarboxylic acids such as TPMA, PMMA, and PEMA (see Table 3 for abbreviations)



**Figure 39** Wet strength: dry strength ratio (left) as a function of acid pickup for three wet strength aids. Folding endurance (right) as a function of the wet strength: dry strength ratio for the same acids. Unbleached kraft pulp was used. For abbreviations, see Table 3 [Xu et al 1998].



**Figure 40** Folding endurance of kraft paper as a function of the W:D ratio for two wet strength aids. EMA = PEMA.

have also been investigated. Xu and Yang (1999) showed that crosslinking cellulose fibres with high Mw PEMA could certainly change the brittleness wet–dry strength relationship, as illustrated in Figure 40.

Despite the promising nature of these results, several factors make these approaches less interesting for practical applications.

Although these additives produce massive wet strength improvements, their cost efficiency is probably limited at practical addition levels compared to commercial wet strength resins. So the practical application of TPMA, PMMA, and PEMA can probably be excluded for economic reasons; PMA is the most practical of these polycarboxylic acids. In all the above investigations, a catalyst was used (Na-hypophosphite). Thus, additions were limited to size press/rod applications, when wet-end additions would be preferred.

Although it appears that fracture resistance can be secured at high wet:dry strength ratios, this does not necessarily mean that creep resistance under moist conditions will be maintained, because cell wall crosslinking is avoided in this approach. Cell wall crosslinking is still believed to be important in decreasing the creep tendency of paper.

#### *Polyethyleneimine, polyvinylamine, and polyallylamines as wet strengthening agents*

It has long been known [see e.g. Allan and Reif 1971; Britt 1981] that certain highly charged polyelectrolytes, such as polyethyleneimine (PEI), can be efficient wet strengthening agents. Oxidation of cellulose also boosts the efficiency of PEI in imparting wet strength [Neogi and Jensen 1980], as more PEI can then be adsorbed. Polyvinylamine [Lorencak et al 1999; Pelton and Hong 2002] is another example of a wet strengthening agent in this class. Oxidation could result in the aldehyde or keto groups on pulps reacting to form imines with these amines. These specific polymers have seldom been used for this purpose, because in terms of cost efficiency they are inferior to other reactive wet strength resins.

#### *Bi- and multilayering as a means of enhancing the efficiency of wet strength agents*

Most wet strengthening agents are cationic, and the maximum amounts of polymer that can be adsorbed under ionic-free conditions correspond to the number of accessible anionic charges (i.e. carboxyl groups) on the fibres. Hence, there is usually a limit to the extent to which the resin can be adsorbed onto the fibres. With bipolar activator technology (CMC grafting) [Laine et al 2000, 2002a,b], the amount of carboxyl groups on the fibres can be enhanced and wet strength can be boosted [Laine et al 2002b]. This is not only because the number of charges increased, but also because PAE resin could react with the carboxyl groups. Multilayering technology [Gardlund et al 2003; Gernandt et al 2003; Wågberg et al 2002] is another technique by which oppositely charged polyelectrolytes can successively be adsorbed onto

the surface of fibres, allowing a large amount of wet strength resin to be adsorbed. If suitable combinations are used, the two polymers may also react with each other, allowing considerable gains in wet strength of paper [Wågberg et al 2002].

*Miscellaneous developments in wet strengthening paper*

There have also been a number of interesting efforts, particularly by Tanaka's research group in Japan, to develop new wet strengthening chemistries, though, to our knowledge, none has come close to producing commercial application. Thus, wet and dry strength improvements achieved by the application of polymers containing isocyanate groups have been reported by Zhang and Tanaka (1999). The same group also investigated copolymers of glycidylmethacrylate and styrene [Zhang and Tanaka 2001a,b], aminated polyacrylamide [Tanaka and Senju 1976a], N-chlorocarbamoylethyl starch [Tanaka and Senju 1976b], and N-chloro-polyacrylamide [Chen and Tanaka 1994, 1996a,b], and found them to have wet strengthening properties. Tanaka has also published some review papers in the field [Tanaka 1994, 1995]. More recently, novel cationic styrene maleimide resins have also been developed in order to bring about wet strengthening of paper [Valton et al 2004].

Recently, the effects of proteins on wet peel strength have been investigated, and a high amount of amino groups was found to be beneficial to wet strength [Xin and Pelton 2004]. In another set of experiments, polyvinylamines (PVAMs) and polypeptides were investigated with respect to their effects on peel strength. Adhesion increased with Mw both for PVAM and the polypeptides. The results pointed to the potential of tyrosine-rich proteins and polypeptides to increase the wet strength of paper [Kurosu and Pelton 2004].

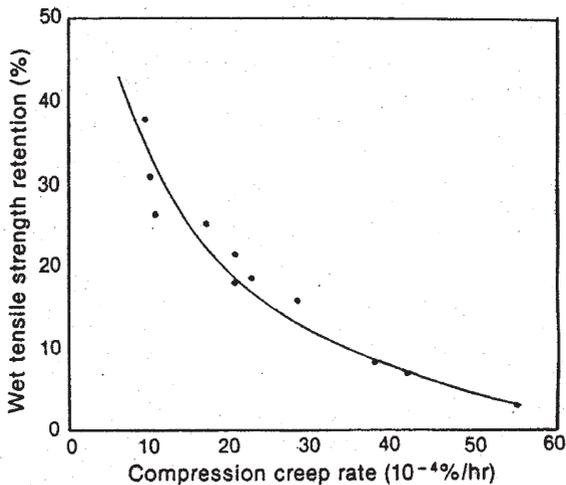
## **PRESS DRYING, IMPULSE DRYING AND CONDEBELT DRYING CONCEPTS AS A MEANS OF DECREASING CREEP IN PAPER**

Press drying, that is, drying a paper while pressing it with a substantial z-directional pressure, was developed at the Forest Products Laboratory in the 1970s by Setterholm and co-workers. This development was followed by extensive investigations in other laboratories because of the strong technical effects recorded [Andersson and Back 1976; Back and Andersson 1979; Horn 1979, 1988; Horn and Setterholm 1983; Horn and Bormett 1985; Seth et al 1985; Setterholm 1979; Setterholm and Koning 1984].

The driving force of this research was the desire to increase the use of

hardwood high-yield pulps in linerboard manufacture. The benefits of press drying were particularly accentuated for high-yield stiff fibres, such as high-yield kraft pulps, which soften under the simultaneous action of pressure and temperature. Other characteristics of press-dried materials are superior dimensional stability and compression creep characteristics when exposed to cyclic humidity [Byrd 1984]. Byrd and Koning (1978) assessed the edgewise compression strength of various conventionally made corrugated samples under conditions of cyclic humidity variation, finding that there were severe limitations to how much the yield of the pulp used could be increased. The benefits of press drying are thus related to the increased sheet consolidation (sheet density) and the restrained drying situation when the sheet is subjected to press drying. Moreover, crosslinking takes place in the cell wall if the wet paper samples are subjected to high temperatures during drying, imparting a significant degree of wet strength to the paper samples. Figure 41 shows the relationship between the wet tensile strength (% of dry strength) versus compression creep rate for samples that were conventionally dried and press-dried at high temperature (204°C).

Work has also been carried out to investigate the molecular mechanisms responsible for press drying. It has been suggested that it is the hemicelluloses that are primarily responsible for the high strength properties associated with press-dried samples, and that the improved compression creep properties of



**Figure 41** Relationship of compression creep rate to wet tensile strength retention in conventionally dried and press-dried handsheets made from high-yield red oak kraft pulp [Horn 1988].

press-dried samples are a result of lignin flow [Byrd 1979; Horn 1979]. Later investigations using the raman microprobe [Atalla et al 1985] indicated considerable cellulose aggregation in press-dried samples.

Extended nip drying of paper became a commercial reality in late 1970s; the idea of impulse drying followed and, in a way, shifted the focus of research from press drying to impulse drying [Gunderson 1992]. Despite the extensive development of the press drying and impulse drying concepts, commercial development stalled because of various technical obstacles. In contrast, Condebelt drying has been put into commercial operation [Huovila 2001; Fellers et al 2003]; hence, Condebelt drying is a most important technology in alleviating creep in paper/board.

## **PHENOL- AND UREA-FORMALDEHYDE RESIN IMPREGNATION**

Impregnation of linerboards and corrugating medium with polymeric resins is a very common method of producing rigid-when-wet corrugated containers [Gupta and Koutitonsky 1994]. Phenol- and urea-formaldehyde resins are the resins most commonly used for this purpose. The board is first impregnated with the resin and dried at normal drying temperatures, after which the resin is cured at high temperatures. The resin may be applied using the liquid applicator system (LAS). A catalyst is also commonly used. Other additives, such as acrylic resins to enhance lignin/starch saturants, sodium silicate-based resin, and aluminium hydroxide gel have also been described in the literature.

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## Transcription of Discussion

# ON THE NATURE OF JOINT STRENGTH IN PAPER – A REVIEW OF DRY AND WET STRENGTH RESINS USED IN PAPER MANUFACTURING

*Tom Lindström,<sup>1</sup> Lars Wågberg<sup>2</sup> and Tomas Larsson<sup>1</sup>*

<sup>1</sup>STFI-Packforsk AB, Box 5604, SE-114 86 Stockholm, Sweden

<sup>2</sup>Dept. of Fibre and Polymer Technology, Royal Institute of Technology  
(KTH), SE-100 44, Stockholm, Sweden

*Dick Hoyland*      University of Manchester

A very simple question. Where has the hydrogen bonding gone? I always thought it was the most important thing holding a piece of paper together?

*Lars Wågberg*

Yes, if you ask the audience here, 95% will say that hydrogen bonding is most important. We have really dug into the literature around this and read all the papers that we have found, by Alfred Nissan and other people. However, it is very hard to find quantitative evaluations where the importance of hydrogen bonding is shown. Personally, I see it as included in the polar part of the work of adhesion and naturally it has a very significant influence on the interaction between fibres.

*Ivan Pikulik*      Paprican

I really enjoyed your review. Here is a minor comment. One of the first graphs you showed was a reproduction from the 1955 paper of M.L. Lyne and W. Gallay on the wet-web strength as a function of solids content. I have seen it

## *Discussion*

reproduced many times. I myself, and my co-workers, have reproduced it in our papers and in our courses. Since then, we have done hundreds of these measurements but we have never seen a saddle in the strength between 30 and 40 % solids. In fact the strength increases somewhat exponentially right through. I am sure that these people have done good work. But they probably use untypical pulps; in fact I know that they used unrefined chemical pulp, which is never used for papermaking. So I just thought I would mention it.

*Lars Wågberg*

Thank you for the comment Ivan, but it has to be stressed that they looked at a range of different types of fibres. I mean both beaten and unbeaten chemical fibres and groundwood fibres as well as, for example, glass fibres.

*Derek Page*

I think it is also a question of looking at the fine print. If you plot something against solids content, you have to ask yourself how was this different solids content reached. Was it by air-drying or was it by pressing? They give different results.

*Theo van de Ven*      McGill University

I have a question about the physical interactions which you say occur in the area of around 50% solid content. You showed a cartoon where you have polymer layers interpenetrating. I guess, if I understand the cellulose surface, those must be hemicelluloses which are usually negatively charged. If that is the case, you would expect a large effect of salts on the interactions and interpenetration. Now, we have recently done experiments as a function of salt and we see absolutely no effect. How would this rhyme with your comments, that you have this interpenetration of hemicellulose chains?

*Lars Wågberg*

Well, maybe I was a bit unclear about that. The system I talked about consisted of polymer multilayers that we formed on a solid surface. For this system we have measured the wet adhesion, in this case not between cellulose surfaces but between a colloidal sphere and a flat surface. For this system we see a definite change in the wet adhesion depending on how we have constructed the layer. Naturally, what you are saying is very valid, but it is also important to consider how the hemicelluloses are deposited on the fibre

surface. Most probably it is a precipitated type of gel that you have on the surface and the interaction, I would guess, would be very dependent on the time of contact between the surfaces and also the degree of swelling of the hemicellulose. In summary, each sphere has to be studied and characterised and from the results the right conclusions must be drawn.

*Artem Kulachenko*      Mid Sweden University

Thank you very much for your presentation. I have a question. Are there situations in which the increased joint strength has an adverse effect on something?

*Lars Wågberg*

That is a very good question, especially if you extend the question to which type of paper property you would like to have. It is important to stress that an increased degree of contact or an increased joint strength can be adverse from a brittleness point of view, for example. You really have to know the final property you want to create and that is also a thing that I did not include. I included a lot from recent work, and I also got a remark from the Chairman on that, but we also have recently seen that you can create both brittle joints and brittle paper if you are not careful in the selection of the chemicals. So, in summary, an increased joint strength is not necessarily very good.

*Alan Button*      Buttonwood Consulting

I was really concerned, until you got down the end, that you were going to totally ignore the mechanical part of this, so I am much relieved by the way you ended. I guess, I would add a point to your mechanical properties and geometry. Some time ago, I did some work which I think clearly shows that you can look at this as a fracture problem using fracture mechanics to describe the strength of the bond. You need in practical papermaking terms to understand the impact that the actual fibre mechanics and the geometry have on the outcome here. What we have with our relative bonded area and bond shear strength approach ignores some of the realities in mechanics here.

*Lars Wågberg*

My comment on that is that the work that I was referring to where we have seen adverse effects at an increased joint strength is exactly what we can see if we compare the results we sometimes get via tensile testing and fracture

## *Discussion*

mechanics evaluation. The fracture properties are determined by how the energy is consumed in front of a crack and this is very different from the results you get from a simple tensile test. So, in short, I agree with you.