Prospects for Maintaining Strength of Paper and Paperboard Products While Using Less Forest Resources: A Review

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Paper production requires large amounts of cellulosic fiber, whereas the world's forested lands and croplands have a finite capacity to supply such resources. To deal with likely future pressure on forest resources, as well as to hold down costs of materials, publications examined in the preparation of this review suggest that the paper industry will need to implement several concurrent strategies. In particular, the industry can be expected to view recycling as a central part of its activities. Basis weights of various paper-based products can be expected to decrease over the coming decades, and more of the fiber content will be replaced with fillers such as calcium carbonate. Such trends will place intense demands upon chemical-based strategies to enhance the bonding within paper and paperboard. Based on the literature, further progress in reducing the amount of new forest resources used to meet a given set of paper product requirements will require a combined approach, taking into account various fiber attributes, nanostructures, novel concepts in bond formation, and advances in the unit operations of papermaking.

Keywords: Decreased virgin fiber utilization; Forest resources; Paper recycling; Papermaking; Dry strength; Filler content; Bonding agents

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INTRODUCTION

This review article is motivated by a deceptively simple question: "Can paper products be successfully manufactured with substantially less freshly-obtained cellulosic fibers?" To the extent that this question can be answered in the affirmative, there is potential either to save costs or to decrease future pressure on the world's forests and other fibrous plants while meeting the requirements of papermakers and their customers. The words "freshly obtained" are included in the question due to the fact that fibers recovered from used paper products can displace some of the need to harvest wood. Emphasis in this review will be placed upon wood resources due to the fact that about 96% of the world's paper production currently involves fibers from wood (RISI 2012), and therefore a great deal of research attention has been focused on wood-derived fibers. There does not seem to be serious cause to be concerned regarding over-use of certain non-wood fiber sources such as sugarcane bagasse (Khakifirooz *et al.* 2013) or wheat straw (Singh *et al.* 2011). In all cases there is still a motivation to increase the amount and strength of paper that can be made from a given amount of fiber resource.

The organisation of this article, after the Introduction, entails four main sections, which deal with (a) factors that limit or hurt the strength of paper, (b) various things that "need to go right" in a papermaking operation in order that the strength of paper approaches its expected level, (c) strategies that show promise to go beyond the present established practices relative to achieving strength goals with less dependence on virgin fibers, and (d) ways in which the unit operations of papermaking might be changed in order to boost strength attributes and allow decreases in the amount of fresh fiber employed.

Whether or not the question posed in the first paragraph is in fact the best question to be asking is a matter that mainly will be left unexamined until near the end of this article. There it will be shown that the published literature is somewhat conflicted regarding the environmental impacts of fiber utilization, including whether recycling of waste paper is environmentally preferable to tree harvesting. Whether and to what extent the utilization of wood resources for papermaking are likely to exceed replacement through photosynthesis are not considered in this article. Evidence suggests that forest resources will continue to be sufficient to meet the near-term needs of papermakers, though not in all regions of the world. While pulping and papermaking practices can have various environmental consequences (Diaz-Balteiro *et al.* 2011; Demel *et al.* 2012), the underlying technologies are based on efficient utilization of renewable materials. In principle, the manufacture of paper can be highly sustainable, from an environmental perspective. Nevertheless, it is reasonable to examine what options may be available to avoid future overutilization of fiber resources, beyond the level at which they can be replaced through environmentally responsible forestry and agricultural practices.

Main Goals

As has been shown by the authors of publications to be considered in this review article, answers to the question of how to achieve paper strength with less use of virgin fibers will turn out to be complex. The required strength characteristics of various paper-based products often pose challenges if one's goal is to reduce the amounts of freshly prepared cellulosic material, *i.e.* virgin fibers. Meeting strength requirements can become even more of a challenge if one considers various ongoing trends, such as increased use of fibers that have been recycled multiple times, greater use of higher-yield, less bondable fibers, greater use of mineral fillers, and decreasing basis weights of various paper and paperboard products (Wielema and Brouwer 2003).

Environmentally friendly approaches

In addition to just avoiding over-use of freshly prepared cellulosic fibers, one also needs to be concerned about net environmental impacts. Paper, when it is manufactured according to conventional practices, is quite durable, easily recyclable, and usually compostable (Hubbe *et al.* 2010; Kumar 2012). Though replacing paper with plastic or metal could be considered as a way to reduce the usage of virgin fibers, such an approach would not address all the underlying environmental issues. The environmental impacts of various strength-enhancing treatments also will need to be considered on a case-by-case basis.

Ways to use less new forest resources

Because it is to their potential economic advantage, papermakers have been striving – practically since paper's invention over 2000 years ago – to achieve comparable strength performance with as little as practical of the cellulosic fibers, which usually have represented a major cost item. One of the most straightforward ways to save on fibers is to reduce the basis weight, *i.e.* the mass of paper per unit area (Gutmann *et al.* 1993; Nordström and Norman 1995c; Hekkert *et al.* 2002; Kerman *et al.* 2009; Li *et al.* 2012b). Notably, all of the articles just cited, except for that of Hekkert *et al.* (2002), had a primary emphasis on how to maintain sufficient product strength when the weight is reduced. Though a great deal of research has been focused on the tensile strength of paper, it is important to keep in mind that other attributes of paper strength can be more important, depending on the application. Many end-uses of paper depend on stiffness and/or compression strength. To maintain stiffness, papermakers often attempt to reduced paper's weight without sacrificing either its thickness or its modulus of elasticity. In the case of paperboard grades, the shear strength within the sheet is often critically important.

Another way to save forest resources is by increasing the yield of the pulping process. In principle if one can use a higher proportion of the raw material in a paper product, then one should expect a corresponding decrease in the demand for the raw material. There are two main categories of pulping processes, mechanical pulping and chemical pulping (Biermann 1996). The pulp from mechanical pulping processes such as thermomechanical pulping (TMP), groundwood pulping, among others, typically comprises over 90% of the starting material, on a solids basis (Sundholm 1998; Kappel 1999). By contrast, the kraft chemical process, which is by far the most dominant pulping method used in the world today, achieves yields in the range of about 40 to 60% of the starting wood material, depending on the wood species and the grade of pulp being made (Biermann 1996; Gullichsen and Fogelholm 1999). Kraft pulping can be very good for the strength of the resulting paper because chemical decomposition and subsequent solubilization of the lignin holding adjacent fibers together in wood makes it possible to separate the fibers from each other in a relatively undamaged condition, conserving the full fiber length. As will be discussed, kraft fibers also tend to have greater ability to form strong inter-fiber bonds compared to most mechanically pulped fibers. The lignin and other materials released from the wood during pulping can be incinerated in a kraft recovery boiler, a process that provides steam energy to help run the pulp and paper operations. By contrast, mechanical pulping operations require huge amounts of electrical energy (Viljakainen 2006).

Increasing the proportion of mineral fillers is a popular strategy that may allow decreased usage of cellulosic fibers. Because mineral products such as calcium carbonate and clay are often less expensive than the fibers that they replace, levels of filler use in various paper grades have tended gradually to increase over a time-scale of decades (Fairchild 1992; Brouillette *et al.* 2010; Doelle and Amaya 2012). Since the intrinsic densities of $CaCO_3$ and clay minerals are substantially higher than those of cellulosic fibers, and also because the mineral products often can pack together more tightly, paper having a high mineral content tends to have a high mass per unit volume – a factor that is often considered undesirable by papermakers. To counter such effects, papermakers have adopted various strategies to keep the apparent density of paper relatively low, depending on the grade of paper being made (Moberg 1985).

The recovery of fibers from used paper products is yet another key strategy that papermakers have employed to conserve forest resources or to save costs. The proportion of recovered fiber that is being used throughout the world for paper manufacture has reached about 54% (Pöyry 2011). In some grades of paper such as containerboard and newsprint paper, the rate of recycling is yet higher. However, it turns out that the process of making kraft fibers into paper, using the paper, and then recycling the used papers, often has the effect of rendering the fibers less conformable when wet, depending on the details of their preparation (Weise 1998). Less conformability can contribute to greater bulkiness of the recycled sheet, which is often just what the papermaker wants when making such grades as printing papers, file folders, and the like. But less conformability also can manifest itself as lower inter-fiber bonding strength.

As noted by Niskanen and Kärenlampi (1998), paper tends to break at locations of greatest weakness. The next section will provide some background on factors that tend to either weaken or limit the strength of paper. Later sections of this article then will examine different approaches that have been evaluated for increasing the strength of paper – thus making it possible to achieve more with less fresh fiber. An underlying theme here is that many things need to be done well simultaneously, since a sheet of paper can fail at many different points and for different reasons.

Critical Mechanical Properties

Before considering factors that either limit or contribute to paper's strength, it is important to consider the widely different physical requirements of different types of paper. This subject has been well covered in the following sources (Scott and Abbot 1995; Mark 2002; Niskanen 2012). Most paper products are required to simultaneously meet several different mechanical requirements. Though tensile strength is among the most commonly evaluated properties, other attributes can be more important with respect to different grades of paper. For example, the mechanical performance of linerboard often can be improved by increasing the tensile stiffness, without necessarily increasing tensile strength, compression strength, or z-directional strength (*i.e.* delamination resistance). Resistance to cracking during folding is another property that is critical for linerboard, and there is often little correlation between such resistance and other strength properties. Bending resistance can be a critical requirement for paper carton board; often such resistance can be achieved most effectively by use of a low-density middle ply. Also, different paper grades can have very different requirements for the ratio of various strength properties in the machine-direction (MD) versus the cross-direction (CD).

FACTORS LIMITING OR HURTING THE STRENGTH OF PAPER

Factors that Tend to Limit Paper's Maximum Strength

The subject of paper strength has been considered in great detail in some previous monographs and key articles. Fundamental aspects, focusing on the structure of fibers and how they attach together during the formation of paper, have been considered (Clark 1973, 1978a,b, 1984; McKenzie 1978; Robinson 1980; Fellers 1986; Htun 1986a). Other sources have dealt with the physics underlying paper strength, focusing on the use of models and equations to represent paper structures and to predict their attributes (Page 1969a; de Ruvo *et al*. 1986; Niskanen *et al.* 1998).

Based on the types of analyses mentioned above, it appears that one of the most pervasive limitations governing paper strength lies in the inherently finite strength of its component fibers. As has been explained by Page (1969a), the strength of paper can depend on the strength of the fibers as well as the strength of the bonds connecting them. Thus, even if one has done a superb job in bonding the fibers together (more on that aspect later), the paper still can fail if the applied tensile or other force exceeds the inherent strength of the fibers, *e.g.* the "zero-span tensile force". Page (1969a) showed that the tensile breaking force (expressed as the length of paper that will break due to its own weight) can be expressed as,

$$1/T = 9/(8Z) + 12\,A\rho g \,/\, [bPL\,(\mathrm{RBA})] \qquad (1)$$

where T is the tensile breaking length (km), Z is the zero-span breaking length (km, usually taken as an indication of the tensile strength of individual fibers), A is the average fiber cross-sectional area, ρ is the density of the fiber material, g is gravitational acceleration, b is the shear bond strength per unit area of intimate contact, L is the length of a fiber, and RBA is the relative bonded area. The RBA is essentially the ratio between the area of fiber surfaces that are intimately attached to adjacent fibers, compared with the total outer surface area of fibers within the sheet. Notably, the first term in Eq. 1 deals with failure due to the strength of individual fibers, whereas the second term deals with failure due to separation of bonded areas.

Interestingly, Mayhood *et al.* (1962) observed a similar limiting strength when evaluating the shear bond strength per unit of bonded area between fibers that had been pressed strongly together in the wet state and allowed to dry. The shear strength per unit of bonded area was found to be almost constant, independent of the type of fibers or how they had been prepared. Thus it appears that there may be an inherent maximum in the strength of a well-formed joint between adjacent fibers in paper. More research of this type, quantifying fiber-to-fiber joint strengths, was reported by Görres *et al.* (1995) and by Fischer *et al.* (2012). Joshi *et al.* (2011) reviewed various studies of this type; their tabulation of results indicates that shear bond strengths based on "fiber crossing" failure tests generally fall within a range between 1.5 and about 8 MPa. The tabulated findings also suggest that different fibers achieve different levels of shear bond strength. Also, differences among the results of different studies tend to cast doubt on whether laboratory-prepared crossings between pairs of fibers are equivalent to what can be achieved within a sheet of paper under realistic conditions of papermaking. There is doubt regarding whether the loading of the individual bond, up to the point of failure, is at all representative of what happens when a paper strip is undergoing a tensile test. Indeed, Joshi *et al.* (2011) obtained higher values of shear bond strength, within the range of 14 to 38 mPa, by using the innovative approach of weakening the fibers in paper sheets by controlled exposure to acid gas. The treatment level was varied such that some of the treated paper showed 100% fiber breakage as a mode of failure along the line of separation.

Ways paper can fail

Paper can fail in different ways, including tensile failure (Page 1969a; Jayaraman and Kortschot 1998), compressive failure such as by crushing or buckling (Seth *et al.* 1979; Fellers 1983, 1986; Paulapuro and Thorp 1983), and by delamination (Fellers 1986; Skowronski 1991; Kang *et al.* 2004). These failure mechanisms each can involve both fiber failure and inter-fiber bond failure. As noted by de Ruvo *et al.* (1986), “Paper is a material with an enormously high degree of heterogeneity containing a seemingly infinite number of cracks of different dimensions.” Thus, the fact that paper can fail is no surprise; rather the challenge is to attempt to come closer and closer to the ideal strength represented by paper’s component parts.

Several authors have considered the concept of “stress concentration,” whereby application of stress to a piece of paper leads to highly nonuniform stresses within the nanostructure of the sheet (Page 1985; de Ruvo *et al.* 1986; Htun 1986a; Tryding and Gustafsson 2000; Kotik *et al.* 2005; Considine *et al.* 2012). As noted by Htun (1986a), the stresses that are manifested at the nano scale, even before force has been applied to the dry sheet of paper, can be attributed to three main sources, the in-plane tensions resulting from drying, additional stresses due to nonuniformities in drying rates, and deformation effects, with emphasis on plastic deformation of the material. One reason why drying tends to impart localized residual stresses within paper is that chemically pulped fibers shrink much more in their cross-direction than in their lengths when they are dried (Salminen *et al*. 1996). Nissan and Sternstein (1964) proposed that only about 10% or less of the hydrogen bonds within a sheet of paper are under a high degree of stress at any time when tensile stresses are imposed on a sample due to the nonuniformity of paper’s structure and the various orientations of the individual bonds. Kato and Cameron (1999) proposed that as the microstructure within paper becomes more organized, the sheet would be expected to become more vulnerable to failure when subjected to a selected degree of expansion, *i.e.* strain. By contrast, a more disorganized structure tends to be better able to absorb the energy of deformation in an elastic manner, not giving rise to localized failure. As proposed by Mayhood *et al.* (1962), it is likely that the initiation of failure involves the detachment of some individual contacts between fibers somewhere within the paper structure. The cited authors noted that such failure was evident when sufficient stress had been applied to approach the end of the elastic region, within which a mainly reversible and quasi-linear relationship between applied stress and observed strain was observable. Acoustic emissions tests have provided one way in which researchers have sought to detect the early events preceding general failure of a stressed paper sample (Yamauchi *et al.* 1990; Gradin *et al.* 1997; Salminen *et al.* 2003; Isaksson and Hägglund 2007). Also, it has been shown that most breakage of individual fibers occurs across the fracture line, and almost no fibers break elsewhere in the stressed sheet (Chiam *et al.* 2013).

Viscoelastic properties and creep

Although the strength components of typical paper products are usually evaluated at temperatures well below their glass transition points, T_g, aspects of viscous flow still have been shown to be very important in certain of paper's applications. As reported by Back and Salmén (1982), the T_g values of both lignin and hemicellulose are strongly depressed by the presence of moisture. Thus it was observed that moist wood-based materials can display viscoelastic behavior at temperatures far below the boiling point of water. By contrast, rigid materials, for which the ambient temperature is below the respective T_g values of the components, can be expected not to show any flow behavior and to experience brittle failure (Wool 2008).

The term "creep" is used to denote a progressive distortion of paper's original shape when tension or compression is applied for a protracted period. Creep behavior can be important when a paper or paperboard product has to sustain a load or stress during its use. For example, the progressive bulging of juice cartons during storage can lead consumers to suspect spoilage of the contents, even if the cause may be more related to the performance of the paperboard. Corrugated containers can gradually sag and eventually buckle when loaded on top of each other in a warehouse (Boonyasarn *et al.* 1992). DeMaio and Patterson (2007) showed that the creep behavior of paper can be modeled according to the conventional "spring and dashpot" models that are widely used in understanding the behavior of other materials. Best fits to data were found when it was assumed that overall creep behavior was due to parallel processes governing initial creep, primary creep, and secondary creep. The authors attributed the non-elastic component of creep to the flow of the matrix components of cellulosic fibers – the hemicellulose and lignin. Htun (1986a) showed that relaxation of an applied stress, at constant length, could be modeled by parallel processes, one governed by an exponential decay law and the other by a power law. Similarly, Kolseth and Ehrnrooth (1986) showed that creep phenomena could be fitted to a combination of initial and logarithmic rate processes.

An especially worrisome type of creep behavior has been observed in some cases when paper-based products are subjected to continuous stress when the humidity is repeatedly cycled back and forth between low and high values (Fellers 1986; Thorpe and Choi 1991). Thorpe and Choi (1991) estimated that containers kept in typical warehouses are able to support only 25% of the loads that would be expected under constant-humidity conditions. Compressive failure of boxes subjected to such conditions was attributed to progressive bending of fibers until build-up of a critical stress at some point within the structure. Haslach (2000, 2009) has reviewed the use of mathematical models and their application in predicting the failure of boxes. Haslach (2009) found that most such failures were ultimately precipitated by fiber pullout and fiber swing, with the release of localized compressive stresses.

Clark (1942) proposed that the flexible, compliant nature of the bonds between fibers may play an important role relative to the toughness and ultimate breaking strengths of paper materials. The idea is that if paper is connected by a series of flexible joints, then an applied load can be transferred throughout the structure and be shared more evenly. Thus, plastic flow may help to explain why paper does not fail earlier than it does (de Ruvo *et al.* 1986). In support of this view, de Ruvo *et al.* (1986) found that there was a low variation of stress within typical paper when placed under tension.

Gimåker *et al.* (2007) showed that short-time creep can be reduced by favorable selection of the wet-end polymer additive used for strength enhancement. Although cationic starch was shown to enhance other strength attributes of sheets made from softwood kraft pulp, it did not reduce instantaneous or time-dependent deformation. By contrast, polyallylamine hydrochloride, a highly charged cationic linear polyelectrolyte, reduced the amount of creep in comparison to the untreated control sheets.

Factors that Reduce Paper's Strength Potential

The factors considered up to this point might be considered as a "best-case scenario," dealing with the limitations on paper strength that are inherent in the fiber materials themselves – even if they are of premium type, quality, and preparation. But to be realistic, a majority of the fibers used by papermakers worldwide are somehow deficient in at least one attribute related to paper strength. To begin with, over half of the mass of pulp used in papermaking comes from the recovery of fiber from wastepaper (Pöyry 2011). Other factors to consider include defects in fibers, losses in the molecular mass of cellulose within the fibers, losses in fibers' ability to swell when placed back into water, the debonding effects of fillers, effects of contaminants, and changes in paper properties due to humidity.

Strength attributes of fibers recovered from wastepaper

Many studies have documented strength losses when cellulosic fibers obtained from the kraft or sulfite pulping processes are made into paper, then redispersed back into water and formed into recycled paper (Pfaler 1933; Brecht 1947; McKee 1971; Cildir and Howarth 1972; Horn 1975; Gurnagul *et al.* 2001; Wan *et al.* 2011). Fuller lists of such studies are provided in reviews of paper recycling (Howard 1990; Ellis and Sendlachek 1993; Nazhad and Pazner 1994; Hubbe *et al.* 2003, 2007c; Nazhad 2005). The greatest relative losses in the bonding ability of such chemical pulp fibers tend to occur during the first cycle of recycling (Göttsching and Stürmer 1978b; Klungness and Caulfield 1982; Van Wyk and Gerischer 1982; Bobalek and Chaturvedi 1989; Hubbe *et al.* 2007c; Yamauchi and Yamamoto 2008; Hamzeh *et al.* 2012). By contrast, mechanical pulps, such as thermomechanical pulp or groundwood pulp used in newspaper production, do not tend to change much from cycle to cycle (Bovin *et al.* 1973; Howard and Bichard 1992; Alanko *et al.* 1995; Law 1996). An exception to this rule is that high-yield pulps that have been chemically treated in some way may also show losses of physical properties of later generations of paper (Ma *et al.* 2012). As noted by Gerspach *et al.* (1993), there is potential for a given fiber to be recycled multiple times, leading to a complex distribution of age of fibers within recycled paper products.

The physical, chemical, or surface-chemical changes responsible for the differences in bonding properties between virgin and recycled fibers appear to be rather subtle (Wistara and Young 1999; Wistara *et al.* 1999). According to the cited studies, recycling of bleached kraft pulps appears to entail a modest reduction in hemicellulose content, which may at least partly explain a reduced swelling ability. No substantial changes in surface chemistry or crystallinity were observed. Thus, one might conclude that physical changes, such as kinks, microcompressions, and pore closure, as well as effects of various contaminants, must be responsible for the reported lower strength of recycled kraft fibers.

Refining has been found to be somewhat effective for restoring the bonding ability of used fibers, except that the additional refining can have a strongly adverse effect on dewatering rates (Bovin *et al.* 1973; Ellis and Sendlachek 1993; Bawden and Kibblewhite 1997; Zhang *et al.* 2004a). The decreased drainage rates appear to be mainly associated with higher levels of cellulosic fine matter (Hubbe and Heitmann 2007), especially in cases where recycled fibers are subjected to a lot of additional refining in an attempt to reach challenging strength targets (Bawden and Kibblewhite 1997). To make matters yet more challenging, if a relatively high level of refining has been applied during the initial cycle of papermaking, then one can expect there to be less possibility to restore bonding within the pulp during subsequent cycles of papermaking (McKee 1971). Cellulosic fines obtained from recovered paper are sometimes considered "dead fines" due to their reduced contribution to inter-fiber bonding (Laivins and Scallan 1993, 1995; Joseleau *et al.* 2012). Some authors have even suggested removing some fines and discarding them as a solution to this dilemma (Cardwell and Alexander 1977; Doshi 1998). However, such a discarding of fine material is seldom done intentionally by papermakers due to concerns about costs of materials and a desire to maximize yields from the process.

The best-known and arguably the dominant cause of strength deficiencies in recycled chemical pulp fibers involves a loss in ability of such fibers to swell when placed into water (Lyne and Gallay 1950; Szwarcsztajn and Przybysz 1976). The popular name for such changes is "hornification" (Jayme 1944). The topic has been discussed by many researchers (Lindström and Carlsson 1982; Guest and Weston 1990; Howard 1990; Nazhad and Pazner 1994; Horn 1995; Weise and Paulapuro 1996; Bawden and Kibblewhite 1997; Cao *et al.* 1998; Scallan 1998; Wiese 1998; Weise and Paulapuro 1999; Hubbe *et al.* 2003, 2007c; Diniz *et al.* 2004; Nazhad 2005; Welf *et al.* 2005; Garg and Singh 2006; Yamauchi and Yamamoto 2008). Gurnagul *et al.* (2001) proposed that a main effect of hornification involves reductions of the shear bond strength, whereas other researchers have more often attributed the effects to reduced relative bonded area. The severity of hornification effects has been found to increase depending on the extent and intensity of drying (Lundberg and de Ruvo 1978a,b; Pycraft and Howarth 1980; Guest and Voss 1983; Hubbe *et al.* 2003; Welf *et al.* 2005), though the main effect has been observed regardless of the conditions of drying of chemical pulp fibers. Baker (2000) notes that the drying of paper, in contrast to the drying of the unrefined pulp, tends to have a more severe negative effect on the reswellability of kraft fibers. Most paper products are dried to the range 2 to 6% moisture content, whereas during the production of dry-lap pulp, the final moisture content can be 10% or higher.

Various factors can influence the susceptibility of different papermaking fibers to the effects of hornification. In the first place, the removal of lignin and some of the hemicellulose from wood material during chemical pulping yields a highly porous structure on a nano-scale. Such pores are susceptible to closure during drying (Stone and Scallan 1966; Berthold and Salmén 1997). Also, a relatively low pH during drying and a relatively low content of residual hemicellulose tend to make the loss of swellability more severe (Lindström and Carlsson 1982). As shown by Hamzeh *et al.* (2012), fibers from juvenile wood (produced when the tree is younger than a critical age) tend to suffer hornification to a greater degree than mature-wood fibers when subjected to the same conditions of preparation, refining, and papermaking. Jahan (2003) and Sheikhi *et al.* (2010) showed that effects of hornification can be seen in non-wood fibers. Maloney *et al.* (1997) showed that some portion of the observed reduction in swellability associated by hornification may already be imparted by wet-pressing, even before the fibers have been subjected to drying. Aarne *et al.* (2012b) found that cationic polyelectrolytes tended to promote irreversible closure of pores in the cell wall having widths greater than about 20 nm; the results were attributed to the suppression of osmotic swelling effects by adsorption of a cationic polyelectrolyte on negatively charged cellulosic surfaces.

De Ruvo and Htun (1983) described the effects of hornification as being essentially the reversal of refining, a process of locking adjacent fibrillar surfaces within the fiber back together after they had been partly delaminated from each other. Such changes might possibly be associated with the increase in size of cellulose crystalline domains during drying, and the effect appears to be brought about by the coalescence or "aggregation" of adjacent cellulose crystallite surfaces (Iyer *et al.* 1991; Newman and Hemmingson 1997; Scallan 1998; Kato and Cameron 1999; Newman 2004; Pönni *et al.* 2012). Newman's (2004) work with ^{13}C nuclear magnetic resonance appears to provide the best evidence that such coalescence of adjacent cellulose crystalline domains can take place during the drying of kraft fibers. Many researchers have concluded that pores within the cell walls of chemical pulp fibers close up in the course of drying, and only some of the pores are readily opened again if the fibers are later placed back in water (Stone and Scallan 1966; Guest and Voss 1983; Berthold and Salmén 1997; Maloney *et al.* 1997; Park *et al.* 2006). Such pore closure effectively collapses the reticular structure within the water-swollen cellulose (Stone and Scallan 1966; Maloney *et al.* 1998a). The closing up of porosity has been confirmed by reduction in the amounts of cationic polymers that can be adsorbed on the fibers from aqueous solution (Gruber *et al.* 1996; Lee and Joo 2000; Hubbe *et al.* 2003). Reductions in the wet flexibility of kraft fibers that have been dried at least once have been documented (Ehrenrooth *et al.* 1977; Paavilainen 1993; Tschirner *et al.* 1998; Cao *et al.* 1999; Dulemba *et al.* 1999; Zhang 2004a). All of these changes can be understood based on the inherent difference between a wooden stick and a cotton rope (Hubbe 2010). Both such structures contain partly-aligned cellulosic fibrillar elements. As noted in Fig. 1, in the case of the stick these elements are fused together due to the lignin between the fibers. In the case of the rope, the cotton fibers are able to slide past one another, thus explaining the much greater flexibility of a rope than a stick.

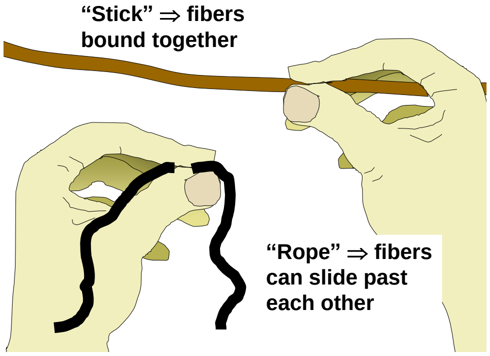

Fig. 1. The difference in behavior between a stick and a rope, which both can be comprised of cellulosic fibers, can be attributed to whether or not the component fibers are fused together.

Wang *et al.* (2003) proposed a mechanism whereby refining in some cases may be expected to render chemically pulped fibers more resistant to loss of swellability upon drying. The authors found that refining of oven-dried bleached kraft softwood fibers yielded a surface area (by the nitrogen adsorption method) that was 7 to 14% lower compared to never-dried pulp exposed to the same refining treatments. When refined to give the same amounts of water in the cell walls, the previously dried pulps exhibited about 12% less cumulative volume of pores smaller than 10 nm, but a correspondingly larger proportion of volume from pores in the intermediate range of 10 to 500 nm. A mechanism that was proposed to explain these findings is illustrated in Fig. 2. As shown, in the native wood one can picture the cellulose micro- or nanofibrils as being held apart by the non-crystalline polymers hemicellulose and lignin. Upon removal of the lignin and a lot of the hemicellulose during pulping, such fibers become susceptible to fibrillar coalescence upon drying (Rebuzzi and Evtuguin 2006; Pönni *et al.* 2012). Refining can be expected to disturb some of the regularity of alignment of nanofibrils within the structure, thus possibly inhibiting coalescence. Evidence to support such a mechanism involves measurements of the crystalline domain sizes (Wang *et al.* 2003; Newman 2004). The described mechanism is also supported by measured changes of the wet flexibility of dried and reslurried unbleached softwood kraft fibers as a function of their refining history. Zhang *et al.* (2004a) reported that the relative decrease in flexibility of the refined fibers was much less than the corresponding decrease in the case of unrefined fibers.

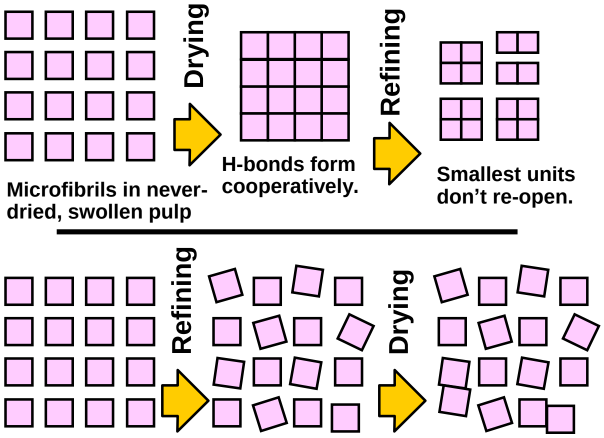

Fig. 2. Schematic illustration of hypothesis to account for an effect of refining the sometimes renders kraft fibers less susceptible to relative loss of flexibility upon drying and rewetting

An alternative or supplementary mechanism to account for hornification involves the possible formation of lactones or ester bonds upon drying of chemical pulp fibers (Diniz *et al.* 2004). The concept is based on the fact that the biosynthesis of each and every monomeric group within cellulose involves lactone formation. It was proposed that formation of additional lactone or ester groups (Ruffini 1966; Slavic and Kucerova 1967) may serve to cross-link and embrittle cellulose-based structures that are heated (Diniz *et al.* 2004). A serious problem with such a mechanism is that it requires there to be a substantial quantity of carboxylic acid groups present in their protonated form in the fibers. Though Lindström and Carlsson (1982) observed substantial hornification of bleached kraft pulps that were prepared in their protonated form, such hornification did not seem to depend on the content of carboxylic acid groups. And though, in principle, esters can form between carboxylic acid groups and –OH groups within a paper sheet, such reactions generally require temperatures that are well above those that are typically used during the drying of paper (Caulfield 1994; Mao and Yang 2001).

Attempts to overcome or avoid hornification by chemical pretreatments of fibers before the paper is dried have been only marginally successful, even in cases where the chemical treatments produced substantial strength benefits due to their action as dry-strength agents (Higgins and McKenzie 1963; Grau *et al.* 1996; Sjöström and Ödberg

1997; Gruber and Weigert 1998; Zhang *et al.* 2001b, 2002, 2004b; Hubbe and Zhang 2005; Mocchiutti *et al.* 2006; Duker *et al.* 2008). Early work of this nature carried out by Higgins and McKenzie (1963) established that changes in the swellability and bonding properties of kraft fibers could be minimized if the paper was dried from a concentrated sugar solution. Other, more technically practical types of treatment failed to prevent loss of swelling upon drying and rewetting. One of the most innovative approaches that have been reported in an attempt to overcome the effects of hornification on bonding involved the application of polyelectrolyte multilayers onto dried fibers, thus reinforcing the bonding zones with substantial quantities of adhesive polyelectrolytes (Torgnysdøtter and Wågberg 2006). In principle, if a sufficiently large amount of adhesive is employed, then even rough and non-compliant fibers can be effectively bonded together (Heerman *et al.* 2006). Many approaches involving polyelectrolyte treatments will be considered later in this article as strategies to make up for and possibly surpass the negative effects of hornification on paper strength.

Strength losses involving cellulose molecular mass

When papermakers wish to predict the quality of a given batch of pulp, one of their most widely used tests is the “viscosity” test, which provides a measure of the molecular mass or “degree of polymerization” (DP) of cellulose within the sample (Nazhad and Pazner 1994). The viscosity of cellulose within fibers is known to decrease during conventional pulping (Suckling *et al.* 2001) and conventional bleaching practices (Fuhrmann *et al.* 1996). As shown by Suckling *et al.* (2001), conventional kraft pulping of pine chips reduced the weight-averaged DP of the cellulose from about 8800 to about 6000 at a final yield of 40 to 50%. With respect to bleaching, Fuhrmann *et al.* (1996) found that the viscosity of the cellulose in softwood kraft pulp fell from 920 to 850 mL/g in the course of a relatively selective bleaching cycle, as the kappa number was decreased from 15 to 2. A more aggressive bleaching sequence reduced the viscosity to 600 mL/g at a kappa number of 2. The corresponding drop in zero-span tensile test, which is representative of fiber strength, was about 15% in relative terms. To provide some perspective on these values, the DP of cellulose within the crystalline regions of cellulose, obtained after acid hydrolysis, lies between 100 and 400 (Battista *et al.* 1956; Kolseth and de Ruvo 1986). Meng *et al.* (2013) showed that related effects can be imparted by the conditions employed during the deinking of pulps; though the molecular mass was not evaluated, the nanostructure of the pulp was profoundly affected.

The cellulose DP also can fall during the aging of paper, especially if the paper has been prepared under acidic conditions (Klungness and Caulfield 1982; Welf *et al.* 1998; Baty *et al.* 2010; Zervos 2010). Though it is not possible to “keep all things equal” when evaluating the effects of cellulose DP on paper strength, it is well known that extensive cleavage of cellulose chains during the accelerated aging of paper results in very poor resistance to folding, *i.e.* extremely brittle paper (McComb and Williams 1981). Kato and Cameron (1999) noted that when paper has been weakened by aging, failure zones tend to be straight and abrupt, consistent with the embrittlement and breakage of fibers, rather than the bonds between them. The fact that paper becomes brittle upon aging, rather than just being weak and limp, suggests a process of coalescence between adjacent fibrils (Newman 2004; Baty *et al.* 2010; Pönni *et al.* 2012). To the extent that such a mechanism is involved, it is likely that a reduced molecular mass of the cellulose, due to hydrolysis, can accelerate the process of microfibrillar coalescence by temporarily increasing the mobility of the individual chains.

Elevated temperature – often with control of humidity – is used in so-called "accelerated aging" tests to determine the relative suitability of different paper products for archival use (Zervos 2010). Pronounced decreases in the degree of polymerization have been observed in some cases, especially during the accelerated aging of papers having acidic pH of the water extract (Klungness and Caulfied 1982; Stephens *et al.* 2008; Zervos 2010). Kato and Cameron (1999) did an analysis to determine whether or not a similar effect might result during the ordinary drying of paper, which entails heating the wet paper in the neighborhood of the boiling point of water. The cited authors concluded that not much chain scission is able to take place during the conventional drying of paper due to the relatively short times during which the paper web is exposed to heat. These conclusions were corroborated by Welf *et al.* (2005). Some results from the latter study are shown replotted in Fig. 3. The data labeled as "wet heating" in the figure corresponds to 15 minutes of exposure of damp kraft fibers to the specified temperatures within a pressure vessel.

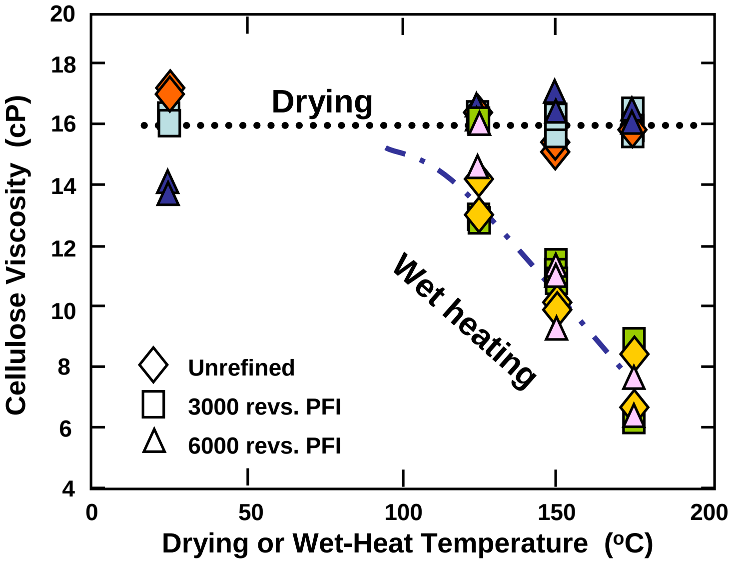

Fig. 3. Effects of temperature on the polymerization degree (as indicated by viscosity) of cellulose in kraft fibers subjected to heating during drying (dotted line, upper) or heating while kept wet (dash-dot line, lower)

Removal of hemicellulose

Another contribution to the loss of the bonding ability of fibers, occurring during various pre-extraction, pulping, and bleaching processes, is the loss of hemicellulose content from the fibers. Pre-extraction of wood chips to remove some of the hemicellulose has been suggested as a potentially beneficial practice, leading to savings in bleaching costs (Al-Dajani and Tschirner 2008; Yoon and van Heiningen 2008). Also, the idea is that the extracted hemicelluloses could be somehow converted into liquid fuels or chemical feedstocks. However, especially if a high proportion of the hemicellulose is removed, researchers have observed substantial losses in the bonding strength of the fibers after subsequent pulping and bleaching procedures had been completed (Oksanen *et al.* 1997; Molin and Teder 2002; Al-Dajani and Tschirner 2008; Yoon and van Heiningen 2008). Thus, there appears to be an inherent conflict of interest between bleaching costs, biofuel opportunities, and the bondability of fibers resulting from a pulping process that incorporates pre-extraction of hemicellulose. To the extent that such systems become implemented, they will tend to increase challenges associated with inter-fiber bonding and susceptibility of the paper to brittle failure.

Defects in fibers

In addition to any loss of swelling, conformability, and bondability, *i.e.* hornification, papermaking fibers also can experience significant mechanical damage at various points during their processing. Such defects, relative to an ideal hypothetical fiber, can include curl, kinks, microcompressions, and weak points (Page 1969b, 1985; Karnis 1993; Omholt 1999). According to Page (1985), a creased or bent section of a fiber cannot be expected to take it full part in transmitting of tensile loading applied to a paper sample. As noted by the cited authors, many such defects can be at least partly reversed by additional refining to swell the fibers and "remove latency". In other words, the fibers are straightened out to some degree (Le Ny and Messmer 2007). The term "microcompressions" is sometimes used to denote abrupt, localized interruptions in the straightness or smoothness of fibers (Nazhad and Pazner 1994; Niskanen and Kärenlampi 1998). Jayaraman and Kortschot (1998) noted that none of the well-established models used to predict paper's breaking strength have attempted to incorporate the effects of fiber defects.

Kontturi and Vuorinen (2009) carried out an innovative study demonstrating a mechanism by which stresses occurring during the drying of paper can induce damage to cellulose nanocrystals within the fiber structure. Such stresses were found to make the nanocrystals more susceptible to hydrolytic attack when the pulp fibers were subjected to concentrated sulfuric acid, using conditions suitable for the preparation of nanocrystalline cellulose. It was proposed that the localized stresses during drying induced strains, possibly within disordered regions between cellulosic crystal domains, thus weakening the material at a nano scale.

Mineral particles (fillers) and paper strength

The adverse effects of mineral additives, such as calcium carbonate and clay particles, on paper strength are well known (Bown 1985a, 1998; Tanaka *et al.* 2001; Li *et al.* 2002). In general terms, such effects have been attributed to the fact that mineral particles at the surfaces of fibers can get in the way of potential bonding interactions between adjacent fibers. It has been found that relatively small filler particles, which can cover more area of fiber surface with a given mass of mineral, tend to have a greater negative effect on strength (Fairchild 1992; Bown 1998a; Li *et al.* 2002; Hubbe 2004). In addition, the interface between the cellulosic material and a mineral surface is always abrupt, never involving intermixing of macromolecule segments and microfibrils from both adjacent surfaces into a three-dimensional adhesive zone.

The tendency of fillers to hold fiber surfaces apart, thereby increasing the amount of air spaces within a paper sheet, can play a distinctly beneficial role in those grades of paper that require increased levels of opacity or brightness (Bown 1998b; Hubbe *et al.* 2008a). Thus, rather than regarding fillers as some kind of "defect", their role in debonding paper is to some extent unavoidable, at least in the case of paper products that require effective scattering of the incident light. Thus, papermakers frequently face the challenge of providing enough dry-strength additive and enough refining action to achieve both goals – a desired bulking effect, which tends to reduce bonded area in the paper, and also sufficient dry strength to meet product requirements.

Contamination

Issues involving "contaminants" are similar, in a way, to the effects of fillers: Something gets in the way of bonding sites, and there is potential for negative effects on paper's strength. But in addition, there are problems due to variability. Levels of contaminants present in a paper machine system are unlikely to remain steady, especially if there are variations in the pulp supply, deinking operations, pulping, or bleaching, *etc.* As noted by Kuys and Zhu (1994), one approach to dealing with variability is to make measurements and attempt to compensate in some way. To give one example, the cited authors recommended the use of online titrations of charge demand of recovered fiber suspensions having variable content of anionic polymeric and colloidal substances. Issues related to charge demand relative to the performance of dry-strength additives and the general operations of paper machine systems have been reviewed elsewhere (Hubbe *et al.* 2012). Strength variations can, in principle, be compensated for by adjustments in refining, by changing the ratio of fiber types, or by adjustment of wet-end additives. In addition, the process engineers who oversee papermaking operations look for deficiencies in washing operations, process control strategies, and alternative sources of supply in order to minimize problems with contaminants.

Monomeric salts, such as sodium sulfate, can adversely affect the performance of wet-end additives such as cationic starch, which is the most widely used dry-strength agent added to the fiber slurry (Beaudoin *et al.* 1995; Ulbrich *et al.* 2012). Such effects become important as the electrical conductivity rises above about 2000 µS/cm. High levels of salt also suppress the swelling of fibers, with a corresponding negative effect on strength (Fält and Wågberg 2003). Though such effects sometimes can be reduced by improvements in washing efficiency (Desharnais *et al.* 2002; Lind 2011), there is a pervasive trend towards higher salt levels in many paper mills. This is because of efforts to reduced usage of fresh water, *i.e.* by multiple reuse of the process water within the paper machine system (Chandra 1997; Huhtamäki 2003; Lee *et al.* 2006). It should be noted, however, that the colloidal and surface-active components often have been found to decrease paper strength properties to a greater extent than inorganic salts (Lee *et al.* 2006).

Surfactants can have either negative or positive effects on paper strength (Touchette and Jenness 1960; Lindqvist *et al.* 2009). Negative effects, when observed, can be attributed partly to a tendency of surfactants to accumulate at phase boundaries – some of which are likely to be the potential bonding sites between fibers during the formation of paper. Also, the reduced surface tension, due to the presence of surfactant molecules at the water surface, will tend to decrease capillary forces that draw fiber surfaces together as the paper is dried. Likely sources of surfactants in a paper machine system include deinking processes, carry-over from pulping and bleaching operations, and a variety of stabilizers used in the formulation of chemical additives. The most serious strength decreases have been observed when cationic surfactants are added to paper machine systems (Touchette and Jenness 1960). This finding is not surprising, given the fact that certain cationic surfactants also are also used as fabric softeners – an application in which they help make cotton cloth feel soft, rather than acting like they are tightly matted together. Certain cationic surfactants have been optimized for the purpose of reducing inter-fiber bonding in certain paper tissue and towel products (Asakura 2003; I'Anson *et al.* 2006). Such debonding agents appear to act by forming hydrophobic patches on the fiber surfaces, so that the net area of bonding is systematically reduced. A similar mechanism, but in an opposite sense, seems to be involved when thermomechanical (TMP) pulps are treated with alkaline solutions (Wegner 1982). Results presented in the cited study are consistent with the removal of hydrophobic wood resins from the TMP fiber surfaces, thus permitting bonding to occur more readily between the more hydrophilic underlying parts of the TMP fibers.

Certain surfactants can have a positive effect on paper strength as a result of their positive effect on water removal during papermaking (Lindqvist *et al.* 2009). The enhanced dewatering was attributed to a lower surface tension, making it easier for suction forces to remove capillary water from between the fibers in paper as the wet web passes over vacuum flatboxes. Also, with less water held within the web before a wet-press nip, the pressing can be more effective in densifying the paper. The surfactant needs to be carefully chosen to avoid stabilization of foam bubbles and entrained air in the system.

Non-linear effects of basis weight reductions

One of the most challenging aspects of attempts to reduce paper's mass per unit area, or "basis weight," while maintaining strength properties, is that the effects tend to be nonlinear. For example, the stiffness of an ideal, uniform, smooth, and isotropic material of constant density can be expected to be proportional to the third power of its mass per unit area (Carson and Popil 2008). Due to the nonidealities of paper, such as the fact that its surface is not completely smooth and contiguous, exponents lower than 3 can be expected to give better fits to stiffness data. Compression strength is another highly non-linear strength property; work reported by Fellers (1983, 1986) has shown that the mechanism tends to shift from one of crushing to one of buckling as basis weight is reduced in a critical range. In both of these instances it would be necessary to increase the elastic modulus (or some other intrinsic measure of strength of the material) by a greater relative amount compared to the desired reduction in basis weight. For instance, one can calculate that to maintain stiffness while decreasing the basis weight by 10%, the Young's modulus would need to be increased by a factor of about $(1/0.9)^3 = 1.37$, *i.e.* about a 37% increase in modulus of elasticity. Another option would be to keep the thickness and modulus constant and increase the specific bonding strength such as to be able to use 10% less material. In theory, an increase of about 54% in the bonding strength might make this possible.

Humidity and moisture

High humidity situations pose some particularly difficult challenges relative to paper's strength (Zauscher *et al.* 1996, 1997). Even in cases where exposure of the paper to liquid water is avoided, high-humidity conditions can cause the paper to lose strength, as well as to stretch or curl as it is used in various applications (Rutland 1992; Taylor 1999; Green 2000).

According to Salmén (1986), all of the main components of wood exhibit rigid behavior under strictly dry conditions unless temperatures are raised above 180 ^{o}C. However, in the presence of water the lignin becomes rubbery within the temperature range 80 to 90 ^{o}C, and hemicellulose is already swollen by water at room temperature. High humidity conditions are sufficient to bring about large changes. The viscoelastic nature of the hemicellulose and lignin within wet or moist wood material at moderate levels of heating make it possible to carry out such processes as thermomechanical pulping (Li *et al.* 2011) and the steam-bending of wood (Wright *et al.* 2013). Meanwhile, though it would be reasonable to expect amorphous regions within the cellulose structure also to swell, evidence suggests that such regions, to the extent that they exist, must be no longer than 4 to 5 anhydroglucose units (Nishiyama *et al.* 2003). Major distortions in the length dimension of cellulosic materials are prevented by the extensive presence of crystalline domains, through which most of the cellulose polymer chains must pass at least once.

Even when paper is dry, under typical conditions of relative humidity, it often contains between about 5% and 8% of moisture content. Some researchers have suggested that the association of such water within the fibers of paper is like a hydrate, something analogous to hydrated forms of minerals (Campbell 1934; Joubert *et al.* 1959; Clark 1984). The term “hydrate” is also supported by the generation of heat when water is added to dry fibers (Maloney *et al.* 1998b). It is not clear to what extent such tightly bonded water can participate in the plasticization of hemicellulose and lignin within papermaking fibers.

The transverse shrinkage and reswelling of a kraft or sulfite fiber during drying and rewetting is typically within the range of 10 to 30% (Page and Tydeman 1962; Larsson and Wågberg 2008). Meanwhile, the length of fibers shrinks by only 1 to 2% upon drying. This contrast in shrinkage tendencies gives rise to some unique effects in paper due to the multiple and intimate contact zones between fibers oriented in different directions from each other. Lateral shrinkage of one fiber has been shown to “crimp” and thus reduce the effective length of a fiber to which it is becoming bonded during the drying process (Page and Tydeman 1962; Baum 1991; Niskanen and Kärenlampi 1998; Kiiskinen *et al.* 2000). Figure 4 illustrates the crimping of fibers within bonded areas, as well as suggesting the effects of such operations as delignification, pulping, and refining on the conformability and ribbon-like shape of kraft fibers in a sheet of paper.

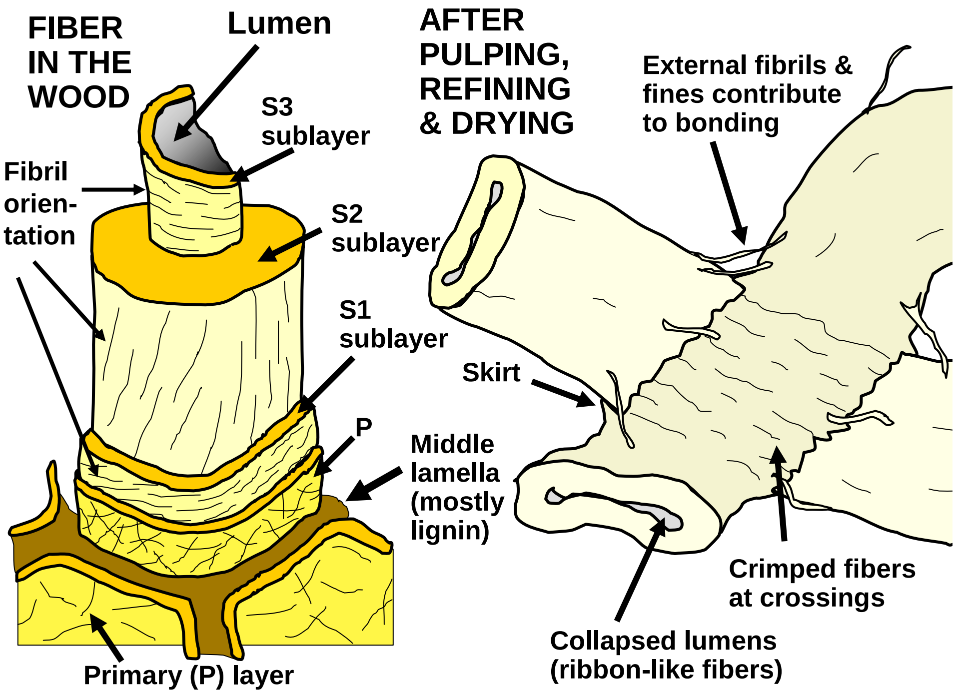

Fig. 4. Illustration of the layered structure of fibers in wood, as well as changes in the shape of fibers in response to kraft pulping, refining, and the drying of a sheet of paper

Drying-induced distortions in the shapes of fibers, including the development of “skirts” adjacent to bonding zones, have been documented (Nanko and Ohsawa 1989; Uesaka and Qi 1994). Such distortions were explained schematically by Lindström *et al.* 2005). Schmied *et al.* (2013) observed that kraft fibers that had been dried in 90-degree contact with each other, then detached by normal force, tended to be smoother in formerly bonded areas, presumably because the adjacent fibers tended to restrain cross-directional shrinkage and related wrinkling. They also observed a higher amount of dangling fibrils in the transition zone between bonded and non-bonded areas after separation of the fibers. The fact that these dangling fibrils had been involved in inter-fiber bonding was evident from the force-distance curves, which indicated progressive failure of bridging elements, one after another. The participation of fibrils in reinforcing inter-fiber bonding is also supported by high-resolution microscopic images of paper surfaces (Nanko and Ohsawa 1989; Fatehi *et al.* 2009b; Schmied *et al.* 2013). Fatehi *et al.* (2009b) observed many fibrillar attachments among fibers in paper formed from bleached sulfite softwood fibers that had been refined. Remarkably, no such fibrillar attachments could be seen in a micrograph representing the same system, but with treatment of the fibers with a high-charge cationic polymer before sheet formation. Presumably the cationic polymer neutralized the charge of the dangling fibrils, causing them to lie down on the wet fiber surfaces.

Some of the dimensional stability problems associated with paper can be traced to the fact that the extent of crimping, as well as its relaxation, are affected by changes in humidity. Indeed, as shown by Uesaka and Qi (1994), the crimping mechanism helps to explain why paper having a high degree of interfiber bonding tends to be more dimensionally unstable and subject to curling when the humidity changes. As noted by Kershaw (1980), a pronounced shrinkage of paper in the course of drying commences just as the amount of water remaining in the paper reaches the fiber saturation point, *i.e.* almost all of the remaining water is within the cell walls of fibers. An additional contribution to the dimensional instability of paper is contributed by the cellulosic fines; according to Przybysz and Czechowski (1985) the dimensions of fines generally have a greater proportional response to changes of humidity in comparison to fibers.

CONTRIBUTIONS TO STRENGTH IN CONVENTIONAL PAPER

Taking Inspiration from the Structure and Performance of Wood

Think for a moment about how truly remarkable are the strength and durability of a typical tree in a forest. Stand next to one that has a trunk about the same size as your own, and you will notice that it towers way above your height. It can stand there patiently, without seemly becoming tired for years and years, while being exposed to occasional strong winds and alternations between freezing cold (in temperate climates), to sweltering heat, and from parched dryness to long stretches of heavy rain. Try holding your arm out perpendicular from your body for even 30 minutes; the tree can do the same for 30 years or more. How does the tree manage to achieve such feats of strength? Clearly it has a lot to do with the details of construction at many different dimensional levels. And because most paper is largely composed of wood-based material, some of what can make paper strong must come from the detailed construction of the woody material itself.

The challenge of understanding and explaining the strength of paper has been taken up in a series of notable articles that generally fall under the classification of "paper physics" (Forman 1950; Page 1969a; de Ruvo *et al.* 1986; Fellers 1986; Kolseth and de Ruvo 1986; Deng and Dodson 1994; Jayaraman and Kortschot 1998; Niskanen *et al.* 1998; Retulainen *et al.* 1998). As noted by these authors, some of the essential aspects that enable the preparation of paper with suitable strength attributes for various applications include macroscopic dimensions, such as fiber length, coarseness, and cell wall thickness. Aspects of the nanostructure are important, including microfibril angle, pore structure, fibrillation (both internal and external), and various organizational aspects such as the uniformity of formation, the presence of fiber flocs, preferential orientation of fibers, and the arrangements of fibrils and cellulosic fines in paper.

To summarize some general findings from the sources cited above, it can be hypothesized that a suitably strong, stiff, but resilient sheet of paper, capable of meeting the requirements of a range of applications, can be created as long as the following criteria are fulfilled:

- Extensive crystallinity within the cellulose component of the fibers contributes to rigidity and resistance to flow; these are attributes that are important in many paper products.
- Amorphous materials, such as the hemicellulose component of fibers contribute sufficient compliance to reduce the susceptibility of paper to brittle failure. It is also reasonable to expect that disordered nanodomains within the cellulose component can contribute to the flexibility of the material.
- There is a well-adapted structure with suitable orientation of cellulose chains, fibrils, and organization of the "matrix" components of lignin and hemicellulose to achieve resistance to failure when stresses are applied to fibers within paper in different directions.
- There is a suitable degree of fiber lumen collapse (so that fibers can be more ribbon-like when present in paper), as well as sufficient straightness of the fibers (except when one wants to prepare paper having high extensibility).
- There is an effective bonding system capable of joining the fibers together with sufficient strength and flexibility, noting that such bonding may involve such factors as the compliance and fibrillation of the fibers, a contribution from the hemicellulose component, and contributions from various dry-strength additives.

Macrostructure

The effects of the dimensions and arrangements of fibers within paper, relative to measurable properties, have been considered in several key studies (Van den Akker 1959, 1969; Page 1969a; Robinson 1980; Fellers 1986; Rigdahl and Hollmark 1986; Jayaraman and Kortschot 1998; Niskanen and Leskela 1997; Yan and Kortschot 1997; Niskanen *et al.* 1998; Considine *et al.* 2012). Some issues to consider initially are fiber straightness, the activation of fiber segments, and visco-elastic effects. The cited studies have shown that it is useful to consider paper as being composed of layers of flattened ribbons arranged mainly in two dimensions. According to Page (1969a), the usual number of crossing points of other fibers on one selected fiber is in the range of about 20 to 40. Thus, even though an individual fiber-to-fiber bond is expected to be much weaker than a fiber, the accumulation of multiple bonds in a well-bonded sheet of paper can be sufficient so that fiber breakage can occur as a major mechanism during tensile failure of a well-bonded sheet. When a strip of paper is being stretched, the force acting along an individual fiber in the loaded network depends strongly on location relative to the fiber's mid-point. The force typically rises from zero at each free end of the fiber to approach a broad maximum at the middle of the fiber. An increase in the number of fiber-fiber bonds will decrease the distance along the fibre required to approach the asymptote. The original derivation is due to Cox (1952).

Fiber dimensions

Depending on the species, genetic differences, the maturity of a tree, and various aspects of growing conditions, the fibers can be quite different in size. To some extent such differences can be the deciding factor governing the selection of a suitable fiber composition for different types of paper product. Softwood fibers, which are often 3 to 4 mm in length and about 30 µm in thickness (Biermann 1996; Nanko *et al.* 2005), can be a good choice when making products that need to resist tearing during their use. By contrast, hardwood fibers, which are often about 1 mm in length and about 20 µm in thickness, are generally preferred for products that need to be smooth and relatively uniform, such as fine printing papers. Fiber length can be critical in light of the multiple contacts between fibers, as mentioned in the previous paragraph. If fibers are too short, then they can be more easily pulled away from each other when tensile stress is applied to the paper. But there is also a penalty for high fiber length; longer fibers are more prone to tangling with each other and forming flocs, which hurt the uniformity of paper. Another important attribute is the cell wall thickness. Thin-walled fibers tend to be more conformable than thick-walled fibers, often leading to greater relative bonded area and higher inter-fiber bonding strength. But thicker-walled fibers tend to be tougher, more tear-resistant, and more capable of withstanding physical abuse. Extensive information about the dimensions of commercially available pulp products is provided by Nanko *et al.* (2005).

Fiber straightness

The relative straightness of the fibers can be expected to play a big role relative to how paper responds to stresses (Page 1985). In a tensile mode, the force required to straighten a fiber can be expected to be much less than the strength required to break the fiber. In addition, when subject to compression, bent fibers will tend to buckle rather than to be crushed (Fellers 1986). In applications where paper might fail in a tensile mode, curled fibers are known to bring about failure of the sheet at lower applied force (de Ruvo and Htun 1983; Rigdahl and Hollmark 1986). Fellers *et al.* (2001) showed that straight bleached kraft fibers were much more effective for the reinforcement of mechanical pulp paper in comparison to curled fibers of the same type. The straight fibers developed higher tensile breaking length than the curly fibers used for reinforcement. Fracture mechanics theory was used to explain the results. Paper products that need to be stiff during their application – such as printing papers – are held under considerable tension during drying by control of the rotational speeds of various rolls and dryer cans (Halme 1967; Maus 1967). Typically the velocity of a paper sheet at the dry end of a paper machine is 5 to 9 percentage points higher than the corresponding value at the forming table (Kershaw 1980); the difference is due to stretching of the sheet during pressing operations and as a result of machine-directional tension during drying

(Baum 1991). Likewise, Halme (1967) estimated that paper typically is stretched by 6 to 8% between the forming section and the exit of the final press nip. Such processes tend to straighten out papermaking fibers during the formation of paper, especially in the case of fibers oriented predominantly in the machine direction.

Page (1985) proposed that kinks and microcompressions within fibers tend to be straightened out in the process of refining fibers that previously had been subjected to drying. The straightening was attributed to both the swelling of the fibers during beating and the tensile forces exerted on individual fibers. Page cited evidence that the strength benefits achieved by refining can be greater than what can be attributed to the observed improvements in bonding strength between fibers in the sheet. A pair of micrographs of a single bleached softwood kraft fiber, comparing the shape of the same fiber before and after refining, showed that the kinks or microcompressions had been effectively removed.

It should be noted, however, that curled fibers can be advantageous when the intent is to prepare relatively weak, bulky structures such as tissue paper or fluff pulp fibers to be used in disposable diapers; for such purposes it is a common practice to employ fresh-dried kraft fibers, which tend to be much more curled in comparison to fibers tried under tension in sheet form (de Ruvo and Htun 1983). As demonstrated by work reviewed by Page (1969b), microcompressions, leading to higher extensibility of the resulting paper, can be induced by carrying out refining at higher consistency levels. Steenberg (1949) noted that paper formed from fibers that are “creased” so that they include a bend between adjacent crossing points with other fibers, can be expected to withstand a greater degree of shock. Thus, when papermakers set out to make tough bags to hold cement and similar products, the processing conditions are optimized to maximize the extensibility of the paper (Edwards and Edmunds 1968; Vishtal and Retulainen 2012; Zeng *et al.* 2013). Such products are typically prepared with a minimum of tension applied during drying, thus allowing the paper structure to shrink and giving it more potential to be later stretched without breakage. Also, tiny bends can be introduced to the paper web during paper processing to achieve related effects (Clupak Inc. 1967).

In the case of cross-machine dimensions, it is possible to somewhat decrease shrinkage of paper during the drying process by control of tension of dryer fabrics, which hold the damp sheet firmly, but intermittently against the steam-heated cylinders (Kiiskinen *et al.* 2000; Linna *et al.* 2002). In ordinary cases the sheet can be expected to shrink in width by at least 2% (Clark 1978c), and in theory by an amount in the range of 1 to 10% (Heikkilä and Paltakari 2000), during drying. Meanwhile the thickness of the paper, which is not subject to any restraint, shrinks by about 30 to 40% (Heikkilä and Paltakari 2000). Hansson *et al.* (1989) showed that cross-directional stiffness and compression strength properties could be improved by an innovative device that prevented cross-directional shrinkage by attaching the edges of a paper web to belts at each side of a paper machine dryer system. A more commonly applied approach, which has been motivated by a desire to minimize web breaks, has involved use of a single dryer fabric, especially in the first dryer section of a paper machine (Kuhasalo *et al.* 2000). As a paper web passes through such a dryer section it remains in contact with just one fabric, rather than having an open draw between each successive dryer can. Such a system at least offers the possibility that friction or temporary adhesion to the fabric surface can inhibit cross-directional shrinkage.

Applied tensions, especially in the machine direction, are believed to minimize the amount of crimping and skirt formation at crossing points between fibers in the paper (Uesaka and Qi 1994). Giertz (1964) introduced the term “activation” to describe a process in which a combination of applied tension, together with the natural shrinkage of fibres during drying, can result in an increase in the proportion of fibers in paper that are straight enough in their segments between crossing points that they fully participate in bearing stress loads. Lobben (1975) used the concept of activation to explain the tensile stiffness of paper. Page (1985) suggested that activation may partly explain the strength benefits of refining once-dried kraft fibers. Vainio and Paulapuro (2007a,b) confirmed the activation concept and showed that fiber segments tend to become straightened when the web is constrained from shrinking during the drying process. Vainio *et al.* (2007) showed that fines from thermomechanical pulp promoted activation by effectively shortening the distances between fiber crossing points within paper. In addition, the TMP fines contributed to more resilient attachments within the wet web, making it easier to strain and thus activate the network without causing too much damage to the fiber-to-fiber bonds. All of these effects promote load-sharing within paper and contribute to higher tensile strength values. Likewise, Retulainen *et al.* (1998) used the term “the Jentzen effect” to describe the irreversible changes within a paper sheet when tension is applied during drying; such effects can include the straightening of fibers and the pulling out of localized wrinkles. Jenztzen (1964) considered the effects of drying on the properties of individual fibers when dried under tension. Such effects can increase the tensile modulus of paper, especially in the machine direction.

Development of bonded area

One of the most unique aspects of the papermaking process is the manner in which adjacent fibers become bonded very tightly to each other over wide areas when the damp sheet of paper is dried. Key theoretical aspects underlying the process of bond formation were explained already by Campbell (1947, 1959) and Forman (1950). The most important aspect of the theory is illustrated in Fig. 5. As shown, one envisions a meniscus of water at a crossing point between two of the fibers, which are represented as planes.

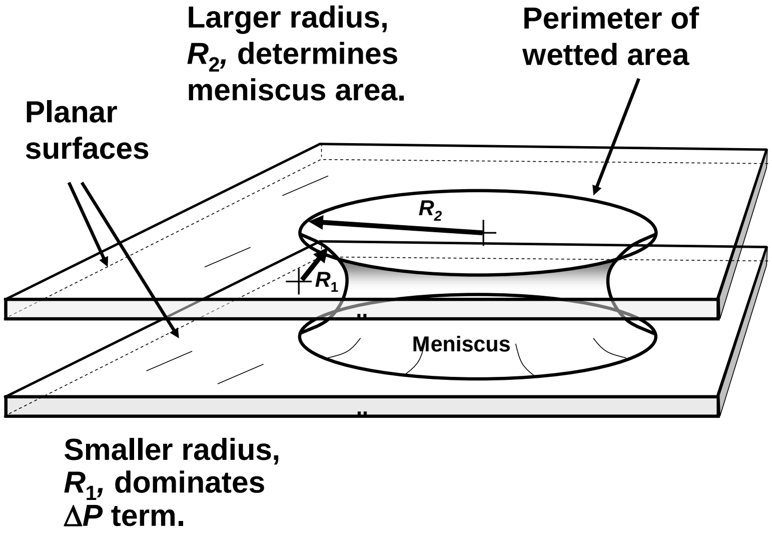

Fig. 5. Diagram of ideal meniscus between smooth planar parallel surfaces, showing the two radii or curvature corresponding to the Young-Laplace equation (Eq. 2).

As water gradually evaporates from the meniscus in the course of drying, a very strong capillary force of attraction draws the fibers so close together that hydrogen bonds can be established (Forman 1950; Campbell 1959; Davison 1980; Robinson 1980). The maximum force can be estimated based on the following assumptions:

- For the sake of simplicity, one treats the two fiber surfaces as if they were perfectly flat and smooth. This turns out to be not a bad model, since the capillary forces are generally large enough to overcome effects of roughness on the surfaces, bringing them into intimate contact. Also, the refining operation renders chemically pulped fibers sufficiently compliant that the lumen spaces collapse, resulting in a ribbon-like shape (Jang and Seth 1998).
- The interfacial tension γ that can be measured by standard techniques is assumed to apply. Though pure water has a γ value of about 72 $\mathrm{mN \cdot m^{-1}}$ at room temperature, lower values can be expected under the situations of interest due to the presence of surface-active substances and higher temperatures.
- It is assumed that the liquid readily wets the surfaces, so that the contact angle θ is significantly less than 90 degrees. Sometimes a value of θ equal to zero is assumed as an approximation.
- The negative pressure within the meniscus is assumed to be equal and opposite to elastic forces acting within the solid material. Such forces act to restore the initial shape that the fiber surfaces had before being subjected to high compression in the wet press and resulting from evaporation of water from each meniscus. Such forces first become prominent when the wet web emerges from the first press nip, such that the capillary forces continue to hold adjacent fibers close together, squashing the original topographies of the two surfaces.
- Finally it is assumed that the outer circumferential border of the meniscus zone exhibits considerable resistance to slippage. Such behavior is consistent with the generally water-loving nature of cellulosic materials, along with the effects of roughness and porosity of the surfaces. Also, as shown by Moss and Retulainen (1997), fiber fines also can play a role in preventing retraction of the bonded area during the drying process.

To the extent that Fig. 5 can be used to model what happens during the drying of paper, the negative pressure (or “vacuum”) within the meniscus zone can be expressed by the Young-Laplace equation (Page 1993; Chen *et al.* 2006),

$$\Delta P = 4\,\gamma\,\cos\theta\,(1/R_1 + 1/R_2) \qquad (2)$$

where γ is the air-water interfacial tension, θ is the contact angle, as measured through the liquid phase, R_1 is the tight radius at the edge of the meniscus, and R_2 is the much larger radius around the outside of the meniscus. One assumes that R_2 becomes very much greater than R_1, especially as water evaporates and the film of water gets very thin. In addition, for simplicity, the value of θ is set to zero. On this basis it is justified, as an approximation, to simplify Eq. (2) as,

$$\Delta P \approx 4\,\gamma\,(1/R_1) \qquad (3)$$

The negative pressure predicted by Eq. 3 tends toward infinity as the last water is evaporated from the meniscus, causing the parameter R_1 to approach zero. Whether the actual pressure differential becomes as high as the predicted maximum value will depend on such factors as the elastic response of the materials, as they attempt to restore the original somewhat rough topographies of the fiber surfaces in the zone of close contact. If one makes the further assumption that the thickness of the meniscus near to its edge is twice the value of R_1, it follows that,

$$\Delta P \approx 2\,\gamma\,/\,x \qquad (4)$$

where x is the thickness of the wetted film. Though it is reasonable to expect that Eq. 4 ceases to be accurate long before the last water has evaporated, the following evidence supports the existence of extremely strong capillary forces drawing fibers together:

- The crimping action described by Lyne and Gallay (1950) requires that the fibers must for some reason be very strongly joined together already before the sheet is dried.
- Studies have shown considerable damage and delamination throughout zones of inter-fiber bonding in cases where the fibers were forcefully detached from each other in the dry state (Page 1960; Sachs and Kuster 1980; Nanko *et al.* 1989; Stratton and Colson 1993). Such damage indicates that molecular contact had been established over wide areas.
- Capillary forces within nano-sized channels have been shown to be sufficiently strong to cause mechanical failure (Tas *et al.* 2010).
- It is hard otherwise to account for the wet-web strength of paper, even before evaporative drying has commenced.
- Assessments of the relative bonded area carried out using visible light of different wavelengths have been found to all give the same results (Page 1960). This observation is consistent with a process that fully closes up any gaps between the adjacent cellulosic surfaces.

In addition to the Young-Laplace contribution to capillary forces drawing cellulosic fibers together after the wet-pressing of paper and during drying, other components of capillary force also have been considered relative to the forming of paper (van de Ven 2008; Tejado and van de Ven 2010). For instance, Fig. 6 illustrates a component of capillary force that helps to explain the initial densification of a paper web on a Foundrinier section of a paper machine up to the point at which air is being pulled through the sheet by application of vacuum from below.

Since no curvature of the meniscus is assumed, the capillary force is given by (van de Ven 2008),

$$F_{\mathrm{cap}} = -2\pi\lambda\gamma D \qquad (5)$$

where λ is a coefficient with a value near to 1, γ is the interfacial tension, and D is the fiber diameter. When summing up all the expected fiber crossings in paper, this component of force was considered by van de Ven (2008) and judged to be at least ten times too small to play a major role in the development of inter-fiber bonding.

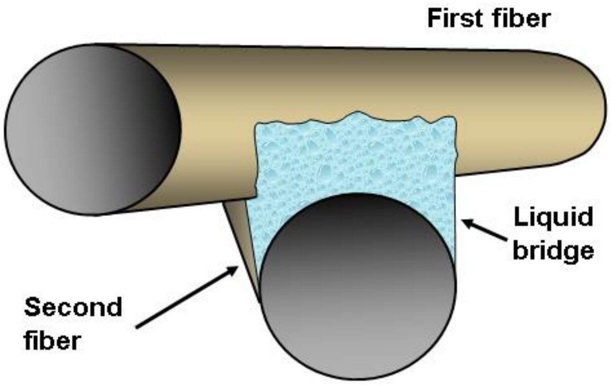

Fig. 6. Illustration of capillary forces acting to densify a wet web of paper as water is being drained out by vacuum and suction from below

Regardless of the detailed mechanisms, the effects of drying on paper properties are dramatic. Figure 7, which is redrawn from the data of Nordman, Levin and Visti, as reported by Kuhasalo *et al* (2000), shows an exponential rise in paper's tensile strength in the dry solids content range between 40% (after pressing) and about 92% (not far from the completion of drying). The right-hand frame of the figures shows that the toughness of the paper, as represented by the tensile energy absorption, went through a distinct maximum at a dry solids content of about 85%. Such behavior is consistent with the decreasing stretchability of paper as it approaches dryness.

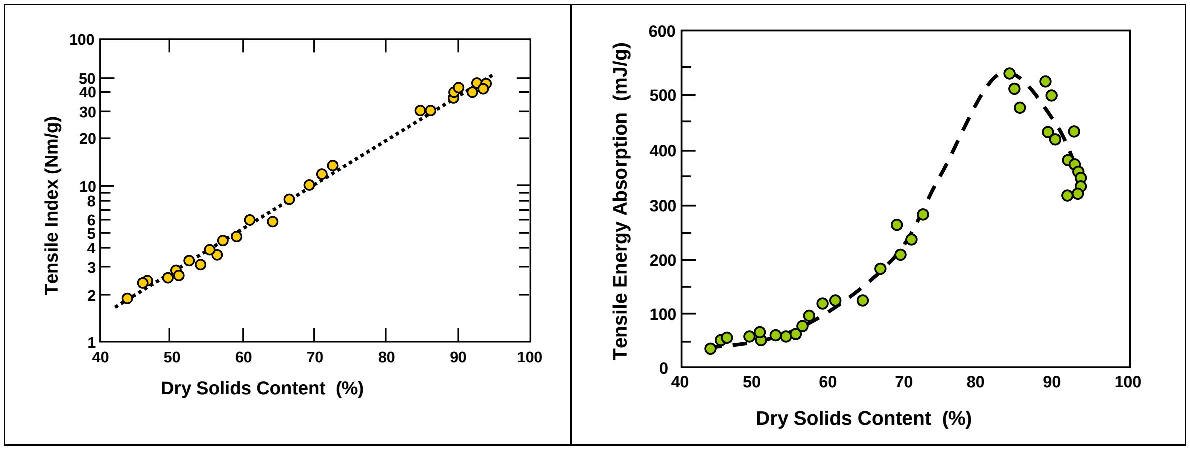

Fig. 7. Tensile stress to breakage (left) and tensile energy absorption to breakage (right) as a function of dry solids content of paper (redrawn from Kuhasalo *et al.* 2000)

Factors affecting the compliance and bondability of fibers

In addition to the critical role played by capillary forces, some other key factors in the formation of bonded areas during papermaking are wet-pressing, the relatively compliant nature of cellulosic fibers that have been prepared by kraft pulping, the further increases in wet-flexibility brought about by refining, and ultimately, the substantial plasticization of hemicellulose and possibly the disordered regions within the cellulose component when exposed to near-boiling temperatures as the damp paper web passes through the dryer section of a paper machine.

The importance of the wet-compliance of a fiber surface in achieving strong bonding has been supported by several studies. As noted by Guest and Weston (1990), paper made from recycled kraft fibers – which tend to be less compliant when wet than freshly-prepared fibers of the same type – generally yield weaker, bulkier sheets, if all other factors are kept constant. In the course of research carried out by Zhang *et al.* (2004b) some unpublished micrographs were obtained showing a pronounced twisting of kraft fibers after they had been formed into paper, then rewetted with water (see Fig. 8). When such fibers were formed again into paper, without further refining, they yielded bulkier and weaker sheets.

A number of authors have reported strong correlations between paper's density and its bond-related strength properties (Robinson 1980; Rigdahl and Hollmark 1986; Guest and Weston 1990; Yamauchi and Hatanaka 2002; Andreasson *et al.* 2003; Asakura 2003). Batchelor and Kibblewhite (2006) found that there is a linear relationship between bonded area and sheet density, provided that fiber cross-sectional area is kept constant. The relationship between sheet density and bonding is considered in detail by Niskanen and Kärenlampi (1998), who showed that greater increases in bonding can be achieved when the paper's apparent density is increased by increasing refining, rather than by application of higher wet-pressing loads. In addition, the densification of dry paper in a calendering nip, as a means of achieving a smoother surfaces, generally does not contribute to bonding. In fact, damage to bonded areas and/or the fibers themselves during calendering tends to reduce the strength of the paper (Hestmo *et al.* 2002; Burnett and l'Anson 2003).

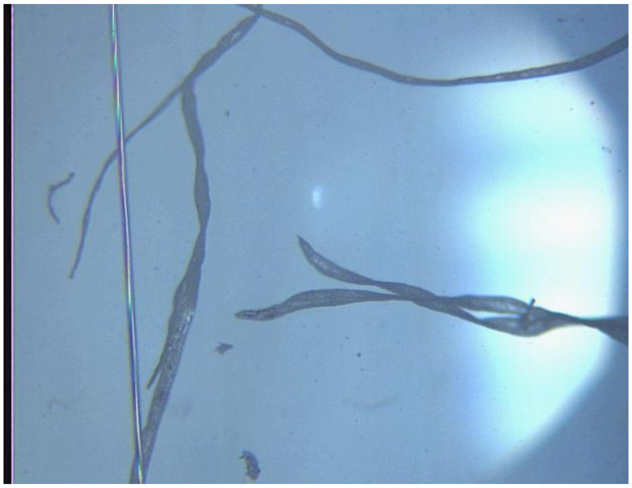

Fig. 8. Micrograph of unbleached softwood kraft fibers that had been made into paper, oven-dried for 12 hours at 105 ^{o}C, then subjected to standard repulping but no further refining (from the work of Zhang *et al.* 2004b, but not published at the time)

The relationship between the porous structure of pulp fibers and paper strength was considered by Andreasson *et al.* (2003). Their study documented increases in the pore volume within wet papermaking fibers as a consequence of lignin removal during pulping. A maximum in pore radius was found at 46% yield when pulping softwood fibers by the kraft process. Further pulping tended to reduce pore sizes, suggesting the commencement of a general relaxing and contraction of the cell wall structures upon removal of most of the lignin and high proportions of hemicellulose from the never-dried fibers. Greatest paper strength was likewise observed at intermediate yield. The authors concluded, however, that the higher strength of such sheets was at least partly attributable to the greater negative surface charge density at the intermediate yield levels. The presence of carboxylic acid groups in the hemicellulose component promotes the swelling of pulp – which is another means by which fibers become flexible and compliant.

Refining and fiber contact

Refining is clearly one of the most important tools to increase the bonding between cellulosic fibers. Already in 1934 Campbell noted that passing a slurry of fibers between a rotor and stator, thereby applying compressing and shearing forces, has the effect of increasing the swelling or "hydration" of fibers. Thode and Ingmanson (1959) found that the strength of paper tended to increase with increases in the swollen specific volume and external surface area of the fibers. Studies have shown that refining tends to increase the swelling of fibers with water, *i.e.* the water retention value; such swelling has been correlated with increased conformability of the fiber surfaces, leading to higher inter-fiber bond strength (Jayme 1944; Ingmanson and Thode 1959; Zhang *et al.* 2004a).

Based on microscopic inspection, one of the most apparent changes that occurs upon refining of kraft fibres is the unraveling of fibrils from the fiber surface. Clark (1978b) proposed that such fibrils play a dominant role in the formation of inter-fiber bonds. Such a view has been partly refuted more recently by studies in which fibers still retained their bonding ability when cellulase enzyme treatment was applied under suitable conditions to remove much of the external fibrils (Bhardway *et al.* 1997; Mansfield and Saddler 1999). Thus, it is likely that a more important aspect of refining is its ability to impart so-called "internal fibrillation" to fibers (Retulainen *et al.* 1998). By internally delaminating the fibers, they naturally become more flexible, as was mentioned earlier. Page (1985) proposed that at least some of the improvement in strength that results from refining of previously-drived fibers may be related to fiber straightness. On the one hand, conventional refining was observed to remove some kinks and curl from fibers, possibly as a consequence of increased swelling. In addition, the subsequent greater shrinkage during the drying of refined fibers might provide greater opportunity for the fibres to be drawn into a straight condition by the time their shape becomes set in the sheet.

Because the cellulose chains and fibrils that contribute to the thin outer-most layers of a woody fiber (*i.e.* the P and S1 layers) generally wrap themselves around the circumference, they tend to restrain swelling of individual fibers suspended in water. So another key function of refining, from the papermaker's standpoint, is that it essentially breaks up those layers, thus allowing the fibers to take up water and become susceptible to internal delamination. It follows that substantial external fibrillation, often leading to the release of fine material, can be considered as an inherent step in the process of getting fibers ready to be formed into paper.

Wet-pressing and the development of bonding

There are many similarities to the effects of refining and of wet-pressing operations during papermaking operations. Wet-pressing, which has been well described elsewhere (Atkins 1979; Back 1987; Mathur *et al.* 1987; Reese 1991; Paulapuro 1993), can be viewed as another approach that results in densification of the sheet and increases in relative bonded area between fibers. An attractive feature of increased wet-pressing, as a strategy to increase paper strength, is that it can result in a lower moisture content of the paper web, which often implies a lower drying energy and a higher rate of production. By contrast, increasing the level of refining can be expected to increase the fines content of the furnish. In the case of a drainage-limited paper machine a slower drainage leads to a lower production rate. The extent of pressing on a given paper machine is often constrained by mechanical factors. In such cases there are a variety of upgrades that have been used in newer paper machines and rebuilds. As will be discussed later in this article, these options include entended-nip presses that provide a longer time for dewatering to take place, while not exceeding levels of pressure that would damage the paper. Conventional wet presses may apply as much as 200 kN/m of linear load, whereas extended nip presses (shoe press) with linear loads up to 1500 kN/m are in industrial use (O'Brian 2002).

Effects of fines on bonding

The degree to which cellulosic fines contribute to paper strength is a somewhat complex subject, in light of fines' strongly negative effect on dewatering when present at relatively high levels in the production high basis weight paper and paperboard (Hubbe and Heitmann 2007; Chen *et al.* 2009). The effects of fines on sheet properties also can depend strongly on the type and bondability of the fines (Niskanen and Kärenlampi 1998). Przybysz and Czechowski (1985) proposed that fines can intensify the capillary effects described by Campbell, thus leading to development of stronger bonds. Some of the most persuasive and interesting evidence supporting the importance of fines was reported by Brecht (1947). His work showed that whereas freshly prepared fines from the refining of kraft pulps can have a strong beneficial effect on paper strength, the fines present in recycled furnish generally do not. This effect was demonstrated by fractionating recycled stock and replacing the "old fines" with "new fines". Properties equivalent to those obtained with virgin kraft pulp in many respects were obtained. Similarly large contrasts in the properties of freshly prepared versus recycled fines have been reported more recently by others (Laivins and Scallan 1993; Olejnik *et al.* 2012).

Formation uniformity

The importance of the uniformity of formation on paper strength has been quite well demonstrated, a least on a scale associated with fibers and fiber flocs. Fundamental works and review articles have described key aspects (Linhart *et al.* 1987; Deng and Dodson 1994; Niskanen and Leskela 1997; Niskanen and Kärenlampi 1998). Also, progress has been achieved in terms of mathematical models to bridge the gap between paper structure and the damage leading to breakage that occurs on a local level within the structure (Korteoja *et al.* 1997; Niskanen and Leskela 1997; Kotik *et al.* 2005; Hagglund and Isaksson 2006). Certain studies that set out to demonstrate benefits of dry-strength additives have shown, probably to the surprise of the researchers, that some effects of the additives could be accounted for based on changes in the uniformity of the resulting paper (Roberts *et al.* 1986; Kim and Hubbe 2010). A study by Linhart *et al.* (1987) provides a particularly persuasive demonstration showing how the addition of retention aids, depending on their type and dosage, reduced the tensile strength of handsheets in a manner that was highly correlated with changes in the degree of fiber flocculation in the sheets. Another way to carry out such a demonstration is to vary the time between agitation of fibers in a handsheet deckle and the drainage of water to form the sheet; delayed drainage produces a much more flocculated sheet that has much lower strength (Norman 1965; Niskanen *et al.* 1998). Retulainen *et al.* (1998) observed that certain effects of formation uniformity on paper strength may become amplified when paper is strained in the wet condition. As was noted earlier, paper tends to be stretched lengthwise by several percentage points between when it leaves the formation section and when it is reeled up (Halme 1967; Kershaw 1980).

Despite the evidence cited above, the relationship between the uniformity of formation and paper strength can be complex. In general a favorable effect of uniform formation is observed when the formation is improved by reducing the consistency of the headbox furnish. This has been shown in the twin-wire roll forming of kraft pulp (Hallgren and Lindström 1989) and recycled pulp (Nordström 2003f). Improved formation through self-healing during dewatering is also associated with an increase in tensile strength (Nordström 2003d). By contrast, tensile properties can be adversely affected when the improved uniformity is achieved by means of pulsations caused by the dewatering blades used in certain twin-wire forming systems (Nordström and Norman 1996; Nordström 2003a; Nordström 2006) or by means of adjusting the jet-to-wire speed difference (Nordström and Norman 1994). The latter effects may be attributed to the partial disruption of the deposited mat of fibers by the imposed flow pulsations, impairing the subsequent establishment of fiber-to-fiber bonds. The flow pulsations may also interfere with the straightness of fibers and their orientation relative to the plane of the sheet. The adverse effects apparently over-ride any favorable effect of blade-induced flows and jet-to-wire adjustments on formation uniformity.

In the case of twin-wire roll-blade forming, the adverse effects of blade dewatering changes the response of the system to forming consistency, as controlled by the headbox flow rate (Nordström 2003b). Formation uniformity and strength both were found to improve with decreasing consistency, but only up to a certain point. Further decrease in consistency beyond that point yielded deterioration in both formation and strength. The latter result was attributed to an increased influence of the blade-induced dewatering, which can be expected to harm the intertwined structure of the wet web.

At a given forming consistency, twin-wire roll forming had been shown to produce substantially better formation that does Fourdrinier forming (Nordström 2003c). The superior results do not depend on an optimization of the jet-to-wire speed difference to achieve the higher strength performance. Rather, the effect may be attributed to the much faster dewatering that takes place in twin-wire forming, making it possible to take advantage of the superior formation uniformity that can be achieved at the outlet of a modern hydraulic headbox. By contrast, the wet web of a Fourdrinier paper machine takes several times as long before the fibers become immobilized as a sheet, giving more time for reflocculation to occur.

Certain aspects of paper strength appear to be somewhat forgiving of nonuniformities in paper that manifest themselves as visible flocs or a cloudy appearance when one holds a sheet of paper up to the light. For instance, Niskanen and Kärenlampi (1998) found that the elastic modulus of paper tends to be self-averaging. Likewise, resistance to delamination, as measured by the internal bond test, seems to be relatively insensitive to the presence of fiber flocs (Odell 2000). By contrast, the force required to break paper in tensile mode has been found to be strongly dependent on the strength of the weakest segments of the paper (Roberts *et al.* 1986; Linhart *et al.* 1987; Korteoja *et al.* 1997; Niskanen and Leskela 1997). Thus, the average tensile strength of paper is decreased if a longer sample from the same source is being tested (Hristopulos and Uesaka 2003; Ora 2012). Values closer to the ultimate potential of the material can be obtained by use of dumbbell-shaped paper strips, forcing breakage to mainly occur within a narrow range of distance (Norman 1986).

Conventional tests of formation uniformity do not appear to be telling the full story with respect to the development of paper strength. For instance, Norman (1986) noted that in certain cases a sheet of paper that appears more floccy, as a result of less hydrofoil action during its formation on a paper machine, can actually exhibit higher strength; such findings were interpreted to mean that something important must be happening relative to sheet formation at a scale smaller than what can be detected by conventional formation analysis methods. It can be expected, for instance, that superior paper strength requires a suitably aligned or interwoven organization of microfibrils or nanofibers in the contact zones between fibers even before the paper is dried. The importance of establishing the detailed structure of overlapping and crossed fibers within paper before drying was made evident by Alince *et al.* (2006); these researchers showed that when pairs of wet blotter papers were pressed together without drying, the strength of the resulting joint was substantially less at the same moisture content than in the case of sheets formed by reslurrying the individual fibers and forming them into a fresh sheet of damp paper having the same solids content.

Fiber preferential alignment

Depending on the type of forming equipment that is used, papermakers have some ability to affect the distribution of orientations of fibers within the plane of the sheet. A tendency for a higher proportion of fibers to be aligned in the machine direction (MD) is called orientation anisotropy. Factors responsible for such isotropy have been considered elsewhere (Norman 1991; Nordström 2003c; Hubbe 2007b). Certain products such as newsprint paper and certain web-offset printing grades require a high degree of MD orientation in order to withstand the high tensions placed on the web during printing at high speeds. Other products, such as certain photocopy papers, tend to perform better when the orientation is close to neutral. In traditional hand-made papermaking such adjustments could be made by optimizing the side-to-side and front-to-back sloshing of the sheet mold during dewatering (Hubbe and Bowden 2009). Certain relatively early models of Fourdrinier paper machines likewise incorporated horizontal shaking of the forming section in an attempt to improve formation uniformity and to encourage more of the fibers to be aligned in the cross direction (CD) (Robertson and Bailey 1934). In modern Fourdrinier papermaking an MD preference can be achieved by a modest mismatch in the jet and wire speeds, though such results are highly dependent on the details of the equipment and furnish being used (Nordström 2003c). In twin-wire roll forming, MD anisotropy can be induced by the elongational strain in the headbox nozzle (Nordström and Norman 1994, 1995b). If high MD anisotropy is desired in roll forming, then a headbox with a high nozzle contraction ratio should be used. Also, long softwood fibers show a larger response to elongational strain in the headbox in comparison to the shorter hardwood fibers (Nordström 2003e). If low anisotropy is desired in roll forming, then a headbox with a low contraction ratio should be used.

Nanostructure

In some respects the nanometer-scale structure of paper may be the most difficult aspect to manage during the papermaking process. The nano-scale organization of fibers already is substantially determined by the growth of the plant, and then to some degree by such processes as pulping, bleaching, and refining. It can be argued that paper owes much of its versatility and resilience to the way in which the cellulose, hemicellulose, and lignin are organized at a nano scale, but the details seem to be largely outside of the ability of papermakers to control what happens. The nano-scale structure of papermaking fibers has been well described (Stone and Scallan 1968; Lindström 1986b). Further, Nissan and Batten (1997) made an attempt to bridge the apparent theoretical gap between macroscopic aspects of paper strength and what happens at a molecular scale. Authors also have explored the implications of models of the fiber surface that involve nano-scale fibrillation (Pang and Gray 1998; Pelton 1993).

Given the central importance of the crystalline regions within the cellulose component of papermaking fibers, it is remarkable how little has been reported about the details of their organization. The degree or crystallization of cellulose within the cell wall has been determined to be somewhere in the range of 45 to 92%, depending on the sample and the method of evaluation (Kolseth and de Ruvo 1986). Cellulose nanocrystals, such as those obtained from cotton by digestion with strong acid or enzymatic treatments, typically have dimensions of about 100 to 300 in length and 8 to 10 nm in width (de Souza Lima and Borsali 2004). A model involving a reticular organization of cellulose (Stone and Scallan 1968) appears to account for many of the observed properties of fibers, especially following their delignification. However, it has not been shown whether or not the crystalline domains of cellulose correspond to the parts of the nanostructure that remain lined up with the fiber axis during the course of such changes as delignification, swelling, and drying.

An even greater degree of uncertainty still seems to persist relative to the nano-scale layout of the non-crystalline parts of cellulose in a fiber. The fact that the average molecular mass of native cellulose in wood is much larger than what has been determined for the molecular mass of cellulose within nanocrystals (Kolseth and de Ruvo 1968) is consistent with a model in which cellulose chains are continuous between crystalline domains and the adjacent disordered regions. Such evidence supports a “fringed micelle” model in which the cellulose nanocrystals within wood are mutually connected by somewhat disorganized zones of cellulose chains (Nishiyama *et al.* 2003). Kolseth and de Ruvo (1986) have suggested that hemicellulose acts as a coupling agent between the cellulose and lignin within a native fiber. The isolation of lignin-carbohydrate complexes (Lawoko *et al.* 2005) supports this view. The layout on a nano-scale does not seem to have been determined.

It has been well demonstrated that mechanical damage to cellulosic fibers under dry conditions is able to convert crystalline cellulose into non-crystalline cellulose. As an example of this, the extensive ball-milling of dry, delignified fibers is capable of reducing crystallinity to a low level (Maier *et al.* 2005; Avolio *et al.* 2012). Kontturi and Vuorinen (2009) found that the drying of paper can induce stress within cellulose fibrils, leading to smaller nanocrystals when the cellulose is digested in strong acid solution. Such damage to cellulose nanocrystals may be just another manifestation of the same interplay between crystallinity and mechanical stressing.

Fibrillar angles within cellulosic fibers

In a manner analogous to the importance of fiber straightness, the predominant orientation angle of cellulose microfibrils within a fiber has been found to play a huge role with respect to strength and dimensional stability of paper (Salmén 1986; Nissan and Batten 1997; Retulainen *et al.* 1998; Courchene *et al.* 2006). Because the S2 sublayer within a fiber typically contributes most of the mass, at least in the case of the wood species most widely used for papermaking, the microfibril origination within that layer has a major effect on the fibers' suitability for papermaking. Courchene *et al.* (2006) found a very strong correlation between the average microfibril angle obtained from otherwise similar loblolly pine trees and the breaking strength, stretch to breakage, and modulus of elasticity of the resulting paper. At the other extreme, Hänninen *et al.* (2011) observed unusual stretching ability in paper sheets made from kraft pulp fibers from juniper trees, a species that is known for having a predominant fiber angle in the range of 22 to 37 degrees from the fiber axis, *i.e.* high deviations from co-linearity. In general, the longitudinal elastic modulus of a fiber can be expected to increase with decreasing microfibril angle in its S2 sublayer (Retulainen *et al.* 1998).

Chemical Aspects of Inter-fiber Bonding

This section will consider what happens at a molecular scale during and after the events described above. The combined effects of pulping, refining, wet-pressing, and capillary forces all can contribute to bringing the fiber surfaces close enough together so that bonding is possible. But without some interaction at the molecular level, the process would not be completed.

Dominance of hydrogen bonding

It is widely agreed that hydrogen bonding plays a central role in holding cellulosic fibers together in a sheet of paper (Forman 1950; Nissan and Sternstein 1964; Nissan *et al.* 1985; Batten and Nissan 1987; Nissan and Batten 1990; Zauscher *et al.* 1996, 1997; Higgins 2002). As explained by Forman (1950), as the last water evaporates from between a pair of fibers, the residual valencies of the hydroxyl groups on the adjacent fibers become mutually satisfied by each other, thus forming hydrogen bonds that join the two fibers together. Additional hydrogen bonds already are at work, acting between and within cellulosic molecular chains in each fiber (Kolseth and de Ruvo 1986; Gross and Chu 2010). Nissan and Batten (1997) showed that macroscopic aspects of paper strength, such as stress-strain curves, could be explained in terms of the stretching of numerous hydrogen bonds throughout the cellulose-based structure. However, due to the different orientations of hydrogen bonds and their varied locations within a paper structure, Nissan and Sternstein (1964) estimated that only about 10% of the hydrogen bonds present would be likely to participate in opposing an applied tensile force. Yuan *et al.* (2013) reported results suggesting that the proportions of hydrogen bonds playing different roles within cellulosic fibers are sensitive to refining. Zauscher *et al.* (1996) showed that a model of paper's elastic modulus based on pervasive hydrogen bonding also was able to account quantitatively for the effects of moisture content and humidity on the measured modulus.

One of the pieces of evidence that is often cited in support of the dominant contribution of hydrogen bonding to paper strength is the fact that extensive incorporation of hydrophobic groups at fiber surfaces tends to decrease bonding strength (Robinson 1980). For instance, acetylation at the 20% level was found to be sufficient to completely eliminate bonding between cellulosic fibers suspended in aqueous solution (Nissan and Higgins 1959). However, this explanation needs to be viewed with caution. As noted by McKenzie (1987) the effect easily could be due to the less swollen and therefore stiffer nature of the derivatized fibers when placed in water. Indeed, it has been found that low levels of acetylation can actually improve the bonding between recycled fibers (Ehrnrooth *et al.* 1977); the affect was attributed to disruption of the regularity of intra-fiber hydrogen bonds.

Various attributes of hydrogen bonds can help to explain paper strength, including paper's sensitivity to moisture and the fact that it is generally easy to recycle. First of all, hydrogen bonding is reversible. Placement of paper back into water allows the hydrogen bonds connecting adjacent fibers to be quickly replaced by fiber-water hydrogen bonds. Second, though hydrogen bonds are roughly a factor of ten weaker than most covalent bonds, based on energy content, they are considerably stronger than the van der Waals interactions upon which materials such as polyethylene depend on so critically. And thirdly, hydrogen bonds are direction-specific. The adjacent groups to be bonded not only need to be close enough, but they also need to be aimed in suitable orientations in order to achieve effective bonding. When this happens as a result of biosynthesis, say during the growth of a tree, it is reasonable to assume that various cellular proteins and organelles play a role in arranging the nanocomponents of wood into a favorable structure to take optimum advantage of hydrogen bonding. When two fibers are thrust together in the course of papermaking, it is not known whether or not nano-scale features have a tendency to align themselves such as to favor a high density and regular organization of hydrogen bonding.

Self-assembly, microfibril coalescence

Campbell (1934) may have been among the first to consider that formation of cellulose chains into crystallites might be involved in the formation of bonding when cellulosic fibers are dried in contact with each other. He stated, for instance, that adjacent cellulose crystallites might "unite if sufficiently close to each other" during the process of evaporation. Newman (2004) presented evidence in support of fibril coalescence and enlargement of crystalline domains in the course of drying and deswelling of kraft fibers during papermaking. Pönni *et al.* (2012) recently reviewed the subject of nano-scale coalescence of cellulose. The high regularity of the cellulose macromolecule can be expected to favor a zipper-like cooperative effect (Lindström 1986b) when cellulose chains happen to be lined up with each other when they are dried in contact. One of characteristics of crystallites, if they are large enough, is that such a structure is unlikely to come apart all at once, even when placed in water.

Coalescence of adjacent crystallites does not appear to play a significant role in joining papers together during the course of ordinary papermaking. If it did, then one would expect to observe substantial development of wet strength even in the absence of wet-strength agents. Since wet-strength development ordinarily requires the use of chemical additives (Espy 1995), it follows that there must be some mechanism tending to inhibit the type of cellulose crystal coalescence that would bind adjacent fibers together in a water-resistant fashion. It is likely that the opportunities for formation of crystallites in the zone of adhesion between adjacent fibers is limited by the presence of materials other than pure cellulose at the surfaces of the adjacent fibers, and also the stringent requirements for alignment in order for adjacent crystallites to "heal together," forming a single unit (Wool 2008). Much more extensive formation of crystallites might be possible if a fully amorphous cellulose, which has to be carefully prepared in the laboratory, were placed in water (Wadehra and Manley 1965). Work by Kontturi *et al.* (2011) showed, however, that certain amorphous cellulose materials can resist conversion to a crystalline form even when they are exposed to water.

Another way to envision a process of self-assembly, possibly in addition to the crystallite-formation process just described, is as an inter-mingling between hydrophilic gel phases. As noted by Pelton (2004), if two water-swollen hydrogel phases are pressed together and then dried in that position, strong bonding will result. The adhesion in such a case can be attributed to some three-dimensional mixing of polymeric chains extending from each of the adjacent surfaces. Such an interaction is consistent with an inter-diffusion mechanism as described by Robinson (1980) and by McKenzie (1984). Pelton and coworkers (2000) later found strong support for such a theory by evaluating the strength adhesion between surfaces that were treated with polymers that were either the same or quite different in terms of their solubility characteristics. The highest strength of bonding was achieved when cellulosic fibers in a slurry all were treated with the same cationic dextran, a very hydrophilic polymer. Quite effective bonding also was achieved if all the fiber surfaces were treated with a somewhat hydrophobic version of the cationic dextran. The lowest bonding strength within the paper was observed when half of the fibers were treated with each of the two contrasting polyelectrolytes. The latter effect is consistent with mutual insolubility of the contrasting types of polymer segments.

The role of conventional dry-strength agents

Because the subject of conventional dry-strength agents such as cationic starch and acrylamide products was covered in a previous review article (Hubbe 2006), only highlights will be included here. Some history of the subject and additional information is provided in earlier reviews of the topic (Clark 1942; Davison 1980; Reynold and Wasser 1980; Ketola and Andersson 1999). Various authors have shown cases in which the addition of dry-strength additives to papermaking furnish has helped them to achieve the stated goal of the present article – to maintain strength properties with less reliance on virgin cellulosic fibers. For instance, dry-strength additives have made it possible to use higher levels of mineral products as fillers in paper (Fineman and Lindström 1985; Tanaka *et al.* 2001; Brouillette *et al.* 2010). Alternatively, the strength of products made from recycled furnish has been improved by such additives (Eichinger 1981; Gaspar 1982; Strazdins 1984; Hipple 1991; Pelton 2004; Mocchiutti *et al.* 2006; Fatehi *et al.* 2010).

To summarize some main points from the articles just cited, dry-strength additives appear to enhance the extent of hydrogen bonding between fiber surfaces. To perform well in this role, the following attributes appear to be important: (a) a highly hydrophilic character with capability of hydrogen bonding; (b) suitable electrostatic charge (either cationic or a combination of cationic and anionic additives) to enable efficient retention at fiber surfaces during papermaking; and (c) sufficiently high molecular mass so that the additive remains at the surface of fibers and does not have sufficient time to become tightly matted down on the surfaces or to permeate into the porosity of the cell wall before the paper is formed. Because many of the effects of dry-strength agents are parallel to those that can be achieved by refining – yielding a stronger, denser, and less compliant sheet - the term "chemical hydration" is sometimes used (Delgado-Fornué *et al.* 2011).

Types of dry-strength agents

Cationic starch is the most widely used dry-strength agent, and many articles have characterized starch's ability to strengthen paper (Roberts *et al.* 1986, 1987; Howard and Jowsey 1989; Alince *et al.* 1990; Glittenberg 1993; Formento *et al.* 1994; Beaudoin *et al.*

1995; Ulbrich *et al.* 2012). Brännvall *et al.* (2007) suggested an innovative approach in which unrefined bleached kraft fibers were pretreated with starch to enhance the bonding properties of dry bales of pulp. To place such wet-end applications in context, it is important to keep in mind that starch products also are frequently applied to the surface of paper in solution form, either at a size press or in a coating operation mixed with clay, calcium carbonate, and other additives of a coating formulation. The usage of cationic starch at the wet end of the paper machine is usually no higher than about 1.5% of the dry weight of solids, whereas the amounts applied at the surface are often larger in such products as printing papers. Cationic starch also is frequently used in combination with other wet-end additives. In particular, sequential addition of cationic starch and colloidal silica products, *i.e.* nanoparticles, can provide a combination of dry-strength improvement and increased dewatering (Swerin *et al.* 1995; Hubbe 2005b; Khosravani and Rahmaninia 2013).

Polysaccharides other than starch also have found use as dry-strength additives (Cushing and Schuman 1959; Rojas and Neuman 1999; Myllytie *et al.* 2009). As noted by Myllytie *et al.* (2009), though some differences have been found between different types of polysaccharides, the overall trends can be expected to be similar. Such findings support the statement given earlier about three key criteria for selection of effective dry-strength agents. Thus, the detailed composition of the material appears to be less important than the combination of hydrophilic character, having an ionic charge, and having a sufficiently high molecular mass.

Synthetic polyelectrolytes, such as acrylamide products, are also used as dry-strength agents. In certain cases the synthetic additives have been reported to achieve high performance (Linke 1968; Chan 1976; Nealy *et al.* 1989; Bhardwaj *et al.* 1997; Carlsson *et al.* 1997; Yamauchi and Hatanaka 2002; Mihara *et al.* 2008; Kerman *et al.* 2009; Sakaemura and Yamauchi 2011). More recently, polyvinylamine and polyallylamine products have come into use (Mocchiutti *et al.* 2011; Marais and Wågberg 2012). Some of the most promising results have been achieved when using amphoteric acrylamide products, *i.e.* polymers that have both positive and negative ionic groups (Tanaka *et al.* 1976; Song *et al.* 2006; Hubbe *et al.* 2007a,b). Such systems will be considered in more detail in a later section.

Carboxymethylcellulose (CMC), despite not being nearly as widely used as a dry-strength additive compared to starch products, has received a great deal of research attention (Horsey 1947; Beghello *et al.* 1997; Laine *et al.* 2000, 2002, 2003a,b; Watanabe *et al.* 2004; Duker and Lindström 2008; Duker *et al.* 2008; Kontturi *et al.* 2008; Aarne *et al.* 2012a). Because CMC has a negative charge, it tends to be repelled from untreated cellulosic fibers in suspension. Therefore, two main approaches have been used to retain CMC as a strength agent. On the one hand, CMC can be added sequentially with a high-charge cationic additive (Gärdlund *et al.* 2003; Hubbe *et al.* 2005; Lofton *et al.* 2005; Fatehi *et al.* 2009a). On the other hand, the CMC treatment can be optimized in terms of the degree of substitution (relatively low charge), ionic strength (relatively high), temperature (relatively high), and time (relatively long) to overcome the electrostatic repulsion (Laine *et al.* 2002, 2003a; Watanabe *et al.* 2004; Duker and Lindström 2008; Aarne *et al.* 2012a). Since each of these approaches offers potential to go beyond the strength performance offered by currently commercialized systems, further discussion will be given later in this article.

According to Zhao and Kwon (2011), dry-strength agents can contribute in two main ways to the effectiveness of inter-fiber bonding within paper, by establishing molecular bonds between the adjacent fibers and by changing the viscoelastic nature of the adhesive joints. It follows that by design and selection of the additives to be used one can achieve effects ranging from strength enhancement to debonding (as might be used to promote softness and bulk in tissue products). Further information about traditional and state-of-the-art wet-end chemical strategies to increase paper strength has been reviewed (Reynolds and Wasser 1980; Scott 1996; Lindström *et al.* 2005; Hubbe 2006).

STRATEGIES TO ENHANCE PAPER STRENGTH

This section focuses on publications evaluating strategies to reach yet higher strength than is ordinarily achieved in current production of paper. In general, papermakers understand that they need to select a suitable mix of fiber types consistent with the strength attributes and other properties required in the respective product. Thus, unbleached softwood kraft fibers would be suitable for making corrugated boxes and paper bags, which need to be very strong, but not for products such as copy paper, which also need to be smooth, fine-textured, and colorless. For cost reasons papermakers often settle for the use of fibers that might be regarded as deficient in some respects; then other measures can be taken to make up for the deficiencies. For instance, it is possible to upgrade recycled fibers and regain some strength performance by such measures as low-intensity refining, alkaline treatments, fractionation to remove some of the fine matter, mixing with some premium-quality fibers, and addition of cationic starch (Nazhad 2005). In the subsections that follow, such approaches will be considered, starting with the macrostructure of paper, then factors affecting the nanostructure of paper, and finally chemical approaches to increasing paper strength beyond what can be achieved with widely commercialized practices.

Table A, which appears in the Appendix, lists the relative increases in paper strength that have been reported in a large number of studies using a wide variety of approaches. When using such information, readers are urged to also consult the cited original publications. That is because the default or “control” conditions considered in different studies can be very different from each other. Some of the most dramatic relative increases in strength have been observed in comparison to weak paper as the default condition. For instance, there may be a low degree of refining or earlier cycles of drying of the fibers. Also, one should bear in mind that various of the individual strategies represented in Table A may be overlapping, mutually exclusive, or inherently incapable of addressing certain other “weak links” that limit the strength of paper.

Macrostructure

The main items to be included under “macrostructure” will be the selection of the fibers to be used, the conditions employed for pulping and bleaching the fibers, considerations in selection of mineral products, surface applications (*e.g.* use of a size press or coater), and ply construction in manufacture of paper or paperboard.

Fiber selection

Fibers can break during the tensile failure of paper, especially in cases where the fibers within the paper are well bonded to each other (van den Akker *et al.* 1958; Helle 1963, 1965; Page 1969a). Information about the strength potential of different kinds of commercially available pulp fibers has been presented by Nanko *et al.* (2005). Looking to the long term, there are opportunities to improve fiber properties by means of tree breeding programs or genetic engineering. This is especially the case for plantation-grown fibers, which in the case of *Eucalyptus* species can have harvest cycles as short as six years (McNabb and Wadouski 1999; Thomas *et al.* 2009). Via *et al.* (2004) reviewed aspects of tree breeding relative to the potential to influence fiber length, coarseness, and pulp quality. Noting that tree breeders often strive for increased density of the wood, it was found that high wood density often correlates with lower stiffness and other strength attributes of the resulting paper. It follows that a new paradigm of tree selection, based on an optimization of other attributes, rather than just a maximization of density, holds promise for improved fiber quality in the distant future.

Microfibril angle, which refers to the orientation of cellulose chains and fibrils within the predominant S2 sublayer of fibers, appears to be a primary determinant of the suitability of different cellulosic fibers for papermaking. For the mainstream of paper products, such as for packaging and printing, species and individual trees having low values of microfibril angle are widely preferred, mainly due to the higher elastic modulus of the resulting paper (Retulainen *et al.* 1998; Courchene *et al.* 2006). In principle, a lower microfibrillar angle could be achieved by selective breeding, by genetic engineering, and by selection and planting of premium trees (Courchene *et al.* 2006).

Older trees, which can be expected to have a higher ratio of mature wood to juvenile wood, are often preferred based on attributes of the fibers (Severo *et al.* 2013). Juvenile wood fibers, which are those that are produced during the first several years of a tree’s life, often tend to have higher microfibril angles, thinner cell walls, and somewhat lower pulping yield in comparison to fibers produced later in a tree’s life. It follows that sawmill residues, which mainly come from the outermost layers or tops of trees, can be considered as a promising source of fibers for papermaking. The time of transition between juvenile and mature wood is highly variable, not only between different tree species, but also dependent on growing condition (Nemeth *et al.* 2008; Mansfield *et al.* 2009). This issue may be of particular importance for short-rotation species such as plantation-grown eucalyptus trees. However, the variability of microfibril angle with age of eucalyptus species (*e.g.* 35 degrees for juvenile *vs.* 10 degrees for mature) tends not to be as great as that associated with softwoods (*e.g.* 15 degrees for juvenile *vs.* 10 degrees for mature) (French *et al.* 2000). One of the goals of some selective breeding programs has been to decrease the microfibril angle in the juvenile wood fibers (Courchene *et al.* 2006). Work reported by Hamzeh *et al.* (2012) showed that juvenile wood also can be more susceptible to strength loss upon its use and recycling.

Pulping

The pulping of cellulosic materials to prepare fibers for papermaking is a huge subject, which fortunately has been well reviewed elsewhere (Biermann 1996; Gullichsen and Fogelholm 1999; Hon 2001; Santos *et al.* 2013), and only some key aspects will need to be highlighted here. For example, it has been found that the potential to achieve certain paper property goals often can be predicted based on the properties of the pulp fibers (Kellogg and Thykeson 1975).

Kraft pulp fibers are generally considered to be superior in strength properties to other kinds of delignified fibers, though the reasons are not completely clear (Page 1983; Young 1994). In the cited reports it is suggested that the difference may be due to the transformation of some partially crystalline regions of cellulose into more fully amorphous micro-domains in the freshly-pulped fibers prior to drying. In other words, a higher ratio of disordered to fully crystalline cellulose content might render the fibers more capable of forming strong inter-fiber bonds upon drying. Further research would be needed both to support the validity of such a hypothesis and also to attempt to somehow engineer superior pulp fibers by manipulating their crystallinity. More recent work by Kontturi and Vuorinen (2006) suggests that low-molecular-mass cellulose at the surface of sulfite pulps and certain other pulps can be a cause of lower tear strength.

Another aspect of kraft pulps that may partly account for their superior strength, compared to various other kinds of pulp, is the degree to which the process is able to minimize physical damage. In principle, the chemical degradation and solubilization of the lignin that binds fibers together makes it possible to liberate the fibers from each other without extensive generation of defects. However it has been shown that even higher strength can be achieved by use of laboratory processing methods that further minimize mechanical damage to fibers during pulping (Hakanen and Hartler 1995).

Selectivity has been a key criterion used by researchers when comparing the value of different pulping and bleaching treatment conditions. Ideally one would prefer that lignin could be removed by pulping and bleaching without causing damage or depletion of the polysaccharide components of the source material. Atalla (1977) showed, for instance, that superior pulp properties could be achieved when using laboratory pulping conditions selected to have an unusually gentle effect on the cellulose and hemicellulose components. Though the conditions employed were not economically attractive, they helped to reveal the extent of unintended damage to fibers that is brought about during conventional kraft pulping. To place matters into perspective, the relatively high strength of kraft pulp, compared to “soda pulping”, for instance, has been attributed to somewhat greater selectivity (Francis *et al.* 2006; Mollabashi *et al.* 2011). Further well-known measures to increase the selectivity of kraft pulping, thus removing lignin with less decrease in yield and/or less degradation of cellulose degree of polymerization, have included polysulfide pulping and the use of anthraquinone, either separately or in combination (Luthe *et al.* 2003; Potucek *et al.* 2005).

Another approach to retaining a greater proportion of the strength inherent in the source fibers has been to increase the yield. In other words, one does not attempt to remove as much of the lignin. As explained by Weise (1998), low-yield cellulosic fibers, from which lignin has been removed, tend to be susceptible to embrittlement and a loss of swellability during drying. Leaving aside the difficulties that a high-yield approach might have relative to the brightness of the resulting pulp, it is reasonable to expect that higher-yield pulp fibers ought to have higher resistance to tensile failure and crushing – especially if those properties are evaluated at a fiber level. Relatively high yield targets are typically used in production of corrugating medium, for which high stiffness and resistance to crushing are critical (Nahrath 2004). In the past, one of the greatest barriers to increasing the yield of kraft pulping processes has been the fact that “under-cooked” chips fail to come apart into fibers when they are blown from the base of a digester at the end of a cooking cycle. Andrews and Hart (2013) showed that such fibers may be released by refining the semi-cooked chips, though the extent of damage to fiber quality can be significant if conditions are not in a suitable range. Sometimes kraft cooking to a relatively high yield is followed by more highly selective bleaching treatments as a means of achieving superior pulp performance and good yield values (Luo *et al.* 2012). As one application of this principle, Nguyen *et al.* (1993) showed that relatively high-yield unbleached kraft fibers obtained from corrugated containers can be subsequently bleached to obtain high-quality pulp suitable for printing grades of paper.

Thermomechanical pulps (TMP) represent another solution that papermakers have developed in past years as a means of preserving fiber length while minimizing the loss of yield. Reme *et al.* (1998) found that stone groundwood pulping has a much greater tendency to break and split fibers, in contrast to the more intact TMP fibers obtained at the same freeness level. On the other hand, when pulping softwood fibers, the TMP process typically yields fiber lengths in the range 1.2 to 1.6 mm, in comparison to about 2.4 mm for the corresponding kraft pulps. The yield of the TMP process is typically well above 90%. Preheating of wood chips with steam, under pressure, softens the lignin component, which has a very high concentration in the middle lamella regions that connect adjacent fibers within wood. Though not achieving as high bonding strength as kraft fibers, TMP fibers are quite resilient with respect to recycling. As shown by various researchers, the fibers can be formed into sheets and reslushed multiple times without loss of swelling characteristics of the fibers or tensile strength of the paper (Howard and Bichard 1992; Law 1996). Göttsching and Stürmer (1978a,b) reported similar findings in the case of groundwood pulp. As noted by Wegner (1982), it is possible to achieve pulp qualities intermediate between conventional TMP and kraft fibers by sulfonation during the mechanical pulping, *i.e.* chemithermomechanical pulping (CTMP). More recently it has become popular to employ alkaline peroxide mechanical pulping (APMP) of hardwoods for production of printings papers (Francis *et al.* 2001; Latibari *et al.* 2012; Muguet *et al.* 2012). Another alternative is to use old newsprint (ONP) and/or old magazine paper (OMP) in applications such as newsprint and light-weight coated products, for which TMP and other mechanical pulps have been customarily used.

Possible interference of lignin with inter-fiber bonding has been an ongoing concern when using high-yield lignocellulosic pulps. Shao and Li (2006) found that lignin at the fiber surface generally tends to reduce the bond strength per unit of bonded area. Wang *et al.* (2011) observed that the surfaces of chemithermomechanical pulp (CTMP) fibers are covered by granules of lignin, whereas the kraft fibers are covered by fibrils composed mainly of the polysaccharide components of wood. Though the lignin appeared to decrease the strength, the latter authors concluded that relative bonded area had a greater effect in determining bonding strength. The relatively poor bonding between polysaccharides and lignin, at least in the absence of naturally formed lignin-polysaccharide complexes (Lawoko *et al.* 2005), is consistent with the great differences in solubility characteristics of the two kinds of materials (Hansen and Bjorkman 1998), which inhibits their three-dimensional interaction when the phases are in contact. However, there has been a scarcity of research aimed at improving the bondability of lignin-covered surfaces in papermaking applications.

With respect to swelling characteristics, Lindström (1986a) showed a strong relationship with pulping yield. The fiber saturation point (FSP) is a measure of how much water can enter the cell walls of fibers. The FSP of wood is typically about 0.4 mL/g (Lindström 1986a). The relatively low value is consistent with the rigidity of lignin in the structure, thus inhibiting the porous structure of cell walls in wood from expanding beyond a certain point. In the case of spruce wood, when some of the lignin and extractives were removed, achieving a pulp yield of 89.3%, the FSP value was increased from an initial 0.5 to 0.8 mL/g. When full delignification was carried out, as would ordinarily happen in the preparation of pulp intended for the production of bleached paper grades, a much higher FSP value of 1.45 mL/g was achieved. These differences help to explain the greater compliance of kraft pulp fibers – especially after refining – so that strong inter-fiber bonding can be achieved.

In principle, one of the most selective ways to carry out specific chemical reactions in lignocellulosic materials is by using purified enzymes. As an example, Liu *et al.* (2013) showed that the strength of paperboard made from unbleached softwood kraft pulps could be increased if the fibers had been functionalized by means of laccase together with either p-hydroxybenzoic acid (HBA), gallic acid (GA), or syringaldehyde (SyA). Such functionalization increased the anionic charge of the fiber surfaces. Lund and Felby (2001) found that laccase treatment improved the strength of unbleached kraft paper only when carried out in the presence of an oxidation mediator. Wong *et al.* (1999, 2000) reported related findings in the cases of high-yield kraft pulp and thermo-mechanical pulp. Widsten and Kandelbauer (2008) presented a thorough review on the subject, in which they came to the general conclusion that laccase treatment can improve strength by enzymatic oxidation, followed by crosslinking of the lignin compounds, especially if the product is heat-cured. Cure temperatures in the range 170 to 200 ^{o}C have been used to achieve the enzyme-induced strength benefits, and it is worth noting that the core temperature of a paper web usually is below the boiling point of water during most of conventional drying on a paper machine (Kiiskinen *et al.* 2000).

Treatment with cellulase can be used to change the properties of refined pulp. If the treatment is done before the pulp is refined, then the main benefit may entail a reduction in energy required to refine to a given level of strength improvement (Seo *et al.* 2000; Heitmann and Wallace 2004; Laothanachareon *et al.* 2011). For instance, Laothanachareon *et al.* (2011) treated old corrugated container (OCC) pulp with a cellulase-rich enzyme mixture. The treatment led to reductions in the energy required for refining, while maintaining compression strength and tensile strength. A more common approach, in the published literature, has been to treat already-refined pulp fibers with cellulase or xylanase enzymes; one of the effects of such treatment has been to increase rates of drainage (Bhat *et al.* 1991; Taleb and Maximino 2007). Pommier *et al.* (1989) showed that it is possible to somewhat over-refine the pulp; then, by carefully selecting the cellulase treatment conditions, it was possible to achieve higher bonding strength at a target freeness level of the pulp. Though Taleb and Maximino (2007) observed an increase in tensile strength following such treatment, there is a danger that over-treatment, due to too high a dosage of cellulase or too long time of contact, can seriously weaken the fibers (Pala *et al.* 2001). Mansfield and Saddler (1999) were able to achieve increases in burst and tensile strength by cellulase treatment, especially if only the long-fiber fraction of a Douglas fir kraft pulp was treated; however, there was clear evidence of fiber damage due to the enzymatic treatment, since the zero-span breaking length values fell strongly upon treatment with cellulase.

Another possible approach that seems interesting, but which is not well enough understood, entails treatment of fibers with deactivated enzyme products. For instance, Pala *et al.* (2001) found that treatment of pulp with enzymatic binding domains, lacking in hydrolytic actifivity, was able to increase both drainage rates and dry strength. Logic would suggest that the increased strength was due to proteinaceous material becoming firmly attached to fiber surfaces and then acting as a bonding agent. Yokota *et al.* (2009) demonstrated the effectiveness of a more ambitious approach, grafting acrylamide polymer chains onto cellulose binding domains and using the resulting compound as a self-retaining dry-strength additive.

Bleaching

Paper technologists do not usually associate the bleaching of pulp with its strength performance. However, the two topics often are related to each other (Annergren 1996). The first thing to be concerned about is degradation of the molecular mass of cellulose chains within the fibers in the course of bleaching. Reduced molecular mass of the cellulose, as indicated by a lower viscosity of its solution, has been correlated with lower tensile strength and tear strength (Annergren 1996). Westermark and Gustafsson (1994) found that whereas the cellulose molecular mass in unbleached birch kraft pulp was relatively uniform, there was a broad distribution and lower mean value of cellulose molecular mass in the same pulp after conventional bleaching.

Laine and Stenius (1997) showed that the selection of a bleaching sequence can affect the surface charge as well as the bonding ability of fibers. In general it was found that a higher negative charge on the bleached pulp resulted in more rapid refining and development of higher bonding strength. Higher charge can be achieved by such strategies as using a bleaching sequence that leaves a high content of hemicellulose in the fibers. As a consequence, bleaching sequences involving a strong oxidizing agent such as chlorine dioxide or ozone, followed by alkaline extraction, tend to remove more anionic charged groups than they generate, thus leaving the fiber in a less charged, less swollen, and less bondable conditions (Laine 1997; Laine and Stenius 1997).

The details of bleaching also can affect how much of the bond-promoting hemicellulose is retained within the pulp (Ratliff 1949). The importance of hemicellulose to inter-fiber bonding is also evident from the fact noted earlier, that excessive pre-extraction of hemicellulose from wood chips can hurt the strength potential of the resulting kraft fibers, even after bleaching (Oksanen *et al.* 1997; Al-Dajani and Tschirner 2008; Yoon and van Heiningen 2008). Helmerius *et al.* (2010) showed that hot-water extraction was particularly effective for extracting hemicellulose form birch wood chips, but pronounced decreases in strength properties resulted. Hamzeh *et al.* (2013) showed that while pre-extraction of hemicellulose from sugarcane bagasse fibers decreased their bonding ability, the strength problem could be overcome by treatment with dry-strength additives before formation of the paper.

Optimization of refining

In view of the very strong relationship between pulp refining and the resulting strength properties of paper, one can expect there to have been many advances in refining technology to achieve better overall results (Bhat *et al.* 1991; Baker 1995; 2000; Batchelor *et al.* 1999; Nazhad 2004; Ghosh 2006; Le Ny and Messmer 2007; Li *et al.* 2011).

As was noted earlier, fibers recovered from used paper products tend to be susceptible to damage, especially if harsh refining conditions are used (Bawden and Kibblewhite 1997; Ghosh 2006). So, as a general rule, such secondary pulps need to be treated gently. One aspect of this is to employ relatively low intensity levels during refining (Wild 1998; Nazhad and Awadel-Karim 2001; Ghosh and Vanderhoek 2001). In other words, one employs a relatively fine pattern of raised bars on the refiner plates, such that the ratio of energy input over the number of crossings of bar edges is relatively low. One should note, however, that intensity alone may be insufficient to characterize the optimum refining treatment (Nazhad 2004). Lundberg and de Ruvo (1978b) showed that high-consistency refining can achieve better drainage characteristics of such pulps after re-refining, consistent with lesser production of cellulosic fines.

Wang *et al.* (2003) showed that refining is not able to completely reverse the effect of loss of swelling due to the drying of pulp fibers. In particular, the crystalline domains in the recycled and re-refined fibers tended to be larger, compared to the crystallite sizes present when the fibers were being formed into the first generation of paper. Interestingly, Wang *et al.* (2003) found that increased refining rendered the fibers somewhat more resistant to pore closure on drying. Related results were obtained by Zhang *et al.* 2004a), who evaluated changes in the flexibility of fibers after they had been dried and rewetted. Refining of the never-dried softwood kraft fibers not only made them more flexible, but also the relative decrease in flexibility upon drying and rewetting was less in comparison to unrefined fibers. Welf *et al.* (2005) found that regardless of the degree of refining of bleached kraft pulps, the water retention value (Jayme 1944) decreased to approximately the same level upon drying. Though the reduction in swelling increased with increasing severity of drying, no memory of the differences in refining were apparent in the WRV data after drying and reslurrying.

Surface sizing

After a paper sheet has been fully formed and is still hot from the drying operation, many paper machine systems – especially when the goal is to produce a suitable product for printing – include a size press operation (Klass 1991; Grön and Rantanen 2000; Maurer 2001). Size press equipment is designed to apply a solution of starch (or other water-soluble polymer or mixture with starch) to the paper surface ahead of a nip between two smooth rolls. The primary purpose of surface sizing, in most cases, is to increase the paper’s strength. For example, Grön and Rantanen (2000) reported increases in the range of 1.4 to 2 in the crush resistance of corrugating medium after surface sizing with starch solution, depending on the basis weight. In addition, depending on the degree to which the paper has been hydrophobically sized to hold the solution out near to the paper surface, the surface strength tends to be increased and the dustiness of the paper is generally decreased. Because the amount of starch applied at the surface can be about 5% of the weight of the paper, for some commodity grades of printing papers, the impacts on strength can be large, sometimes dwarfing the effect of cationic starch added at the wet end of a paper machine.

An area of innovation, with potential to increase the strength benefits of surface sizing, has involved supplementary use of various synthetic polymer additives to the size press. For instance, a water-borne epoxy resin added at the size press with starch has shown promise for increasing the strength and stiffness of low basis weight paper (Li *et al.* 2012b). Alternatively, promising strength improvements have been achieved by the addition of latex products at the size press (Yan *et al.* 2013).

Given such promising results that have been achieved with size-press addition of strengthening agents, one might ask why don’t all paper machines have size presses. For many grades of paper, the answer comes down to money and limitations on the production rate. Use of a size press entails at least some re-wetting of the paper, so the sheet needs to be dried for a second time. In a typical size press operation, the dry content of the web falls from about 95-98% down to about 65-75% (Kuhasalo *et al.* 2000). The need to redry the paper after the size press usually implies that the overall rate of production is much lower than what could have been achieved if the size press operation had been bypassed. In addition, any nonuniformities in rewetting of the sheet at the size press can be expected to adversely affect the flatness and the uniformity of tension within the paper after the second cycle of drying.

Another question that can be asked is, “As long as the paper web becomes rewetted at a conventional size press, why not completely saturate the paper with a solution of strength-enhancing additives?” Such a question was considered by Jopson (1993). Based on test results it was suggested to saturate paperboard for corrugated containers with use of moisture-resistant, thermoplastic binders in combination with starch products. A pressure saturating system, based on wetting one side of the board as the web follows the circumference of a roll, was found to be more effective than conventional size-press systems for applying a lot of solution at high basis weights.

In cases where a way can be found to eliminate the need for and to bypass size press, such a change has the potential to increase the rate of production on a dryer-limited paper machine. Such an approach was suggested by Brouwer (1997), who showed that a certain combination of wet-end additives was able to achieve strength benefits equivalent to those of size-press starch addition in certain cases. Another strategy to minimize the need to re-dry the paper involves adding less water during surface sizing. Thus, Lipponen *et al.* (2004) showed that a size press could be run with a starch concentration as high as 18% solids, and that it was still possible to keep the degree of polymerization high enough to achieve strength benefits.

Ply construction of paper products

Increased stiffness, as well as various other desired attributes, can be achieved when using paper machine systems that are set up to form multiple plies. Though this is not a new technology, there is still considerable potential for more widespread implementation. The most commonly employed strategy employs strong, well-refined fibers in the outer plies, while cheap, bulky fibers, often with lower bonding ability, are placed in an inner ply or plies (Navaee-Ardeh and Nazhad 2008). Bristow and Pauler (1983) described relatively early efforts to extend multi-ply technology to the basis weight range of conventional paper products. Notably, it was shown that the greatest tensile strength and resistance to tearing could be achieved if the usual arrangement of fibers were reversed, placing the highly bondable, long fibers in the center of the structure, and placing the bulky, less bondable fibers in the outside layers. However, in printing papers it is more common to engineer the sheet so as to maximize filler content while achieving the specified stiffness and smoothness at a specified caliper and basis weight.

Corrugated construction of paper and paperboard

Corrugated construction might be regarded as a way to “cheat” and to achieve strength attributes beyond what can be achieved in an ordinary sheet of paper – even a sheet composed of multiple plies (Bi 2012). The basic product is assembled from two linerboard layers, a corrugated layer of “fluting medium”, and some means to adhere the components together, *e.g.* starch adhesive. The corrugated board product takes advantage of an “I-beam” type of construction, in which the high-modulus linerboard layers are held apart from each other. Such a system can provide a high resistance to bending. Corrugated paperboard has enjoyed a dominant position for many years in the production of single-use, recyclable shipping containers (Twede 2008).

One trend that merits watching is the degree to which corrugated construction may increasingly compete with lower-weight products (Brunauer 2004). Such products, which have been used especially in the packaging of some fast-food items, involve the use of much finer ply construction and finer corrugations (Brunauer 2004). Notably, the kind of test procedures that have been used in the past to characterize the strength of corrugated board products do not appear to work as well in testing of these finer corrugated products (Wilson and Frank 2009). Localized buckling, which depends on the flatness of the liners, becomes a major mode of failure as the liner weight is decreased (Popil 2012).

Optimization of the Nanostructure

There is considerable evidence that paper strength depends on structures formed at the nanometer scale during the ordinary papermaking processes. High resolution imaging has revealed the importance of nano-scale structures, including very narrow fibrils and fines, in the bonding zones of paper (Nanko and Ohsawa 1989; Nanko *et al.* 1989; Stratton and Colson 1993; Kang *et al.* 2004). Various imaging studies have revealed nano-sized cellulosic fibrils that apparently assist in the bonding between adjacent fibers in a typical sheet of paper (Mayhood *et al.* 1962; Clark 1978a,b; Moss and Retulainen 1997; Schmied *et al.* 2013).

Mihara *et al.* (2008) showed that paper strength properties can differ depending on the details of where strength additives are located, including at the surfaces of fibers or concentrated at the edges of bonded areas. Conventional wet-end addition was found to favor accumulation of an acrylamide-type dry-strength polymer generally over the surfaces of kraft fibers, and to some extent permeated within the cell walls of the fibers. Due to the bonding agent being present between fibers at each point, one might expect wet-end addition to favor increasing strength of bonding within the bonded areas. By contrast, addition of the strength-enhancing polymer by external application, *i.e.* by means of a size press, allowed the dissolved polymeric material to become concentrated during the evaporation of water. Because a meniscus of aqueous fluid between fibers tends to recede towards crevices such as bonded areas during evaporation, one can expect a reinforcement of the edges of such bonds (Pelton *et al.* 2003; Pelton 2004). Since either one of these models can be expected to increase the strength of paper, it is not clear which mechanism might be judged to be more effective in a given circumstance.

The location of bonding agents on fibers *vs.* cellulosic fines also has been shown to make a big difference relative to paper strength (Strazdins 1980; Stratton 1989). Each of these studies showed that placement of the bonding agents on the surfaces of fibers rather than on cellulosic fines tended to yield higher strength. However, to achieve such placement, each of the cited studies employed fractionation of the furnish, followed by selective treatments and then recombination of the fines and fibres. Because fractionation would entail additional equipment and operating expenses, such procedures are almost never carried out at a commercial scale. Fortunately, there is a practical way to at least partly achieve some of the expected benefits. That is, the ratio of fine matter to fibers tends to be somewhat lower if the pulp stream is treated prior to its dilution at a fan pump. Fines tend to be enriched in the “thin stock loop” of a conventional paper machine due to the fact that some of the fines are not retained on the forming fabric and get recirculated in the “white water” returning to the fan pump. For this reason it is a common practice to add cationic starch and other dry-strength agents to thick stock so that it can become adsorbed onto the fibers shortly before the stock is diluted at a fan pump.

Nano-scale aspects of filler use and paper properties

The mineral products that are widely used in papermaking tend to have overall diameters in the range of about 1 to 5 µm, which is too large to justify use of the term “nano-scale”. However, it turns out that some of the most widely used filler products, *i.e.* the scalenohedral or “rosette” form of precipitated calcium carbonate (PCC), are actually fused-together structures composed of yet smaller parts (Gill and Scott 1987; Fairchild 1992; Hubbe 2004). The reason that rosette-type PCC has become very popular can be traced to its low packing density and bulky structure (Gill and Scott 1987). Because mineral products, *i.e.* “fillers” used in papermaking, typically have a much higher intrinsic density than the cellulosic fibers, and also due to their strong debonding effect, as noted earlier, it is important to consider ways in which papermakers have dealt with these issues. Though papermakers have always had a strong incentive to replace some of the fibers in paper’s composition with something cheaper, it is still necessary to meet customer requirements for the expected thickness (*i.e.* “caliper”) and strength properties. Even though filler particles are much smaller than the fibers in a typical piece of paper, a bulky filler structure can tend to brace sections of the fibers farther part from each other, thus increasing the caliper of the paper. Then the paper typically has to pass through calendering nips to achieve the required smoothness, depending on the expectations of the customers. When using a filler product that has a bulky composite structure, it can be easier to maintain the caliper at least as high as the required minimum value. Although, in general, a bulky type of filler tends to have a greater debonding effect on paper (Gill 1989), such effects can be at least partly compensated by use of cationic starch and other bonding agents at the wet end (Lindström and Florén 1984; Lindström *et al.* 1985; Alince *et al.* 1990; Tanaka *et al.* 2001; Sang *et al.* 2011), as well as application of size-press starch to the paper’s surface (Gerli *et al.* 2011).

Another type of structuring occurs when mineral particles are agglomerated together, usually as a result of treatment with a solution of cationic acrylamide copolymer or cationic starch (Riddell *et al.* 1976; Brooks and Meagher 1982; Stark *et al.* 1987; Shen *et al*. 2009; Sang *et al.* 2012; Seo *et al.* 2012). Such agglomeration leads to an effective increase in the size – and a concurrent decrease in the effective number of filler particles, such that a greater proportion of the fiber surfaces can be expected to remain uncovered and available for strong inter-fiber bonding. In addition, the somewhat flexible nature of the agglomerates held together by flocculating polymers means that the fibers are not braced apart nearly to the same degree as it would be in an equivalent case with highly rigid agglomerates, as might be created by the same nominal size of agglomerates formed by a calcination or crystallization process.

Filler also can be agglomerated together with cellulosic fines. Subramanian *et al.* (2008) and Lin *et al.* (2010) showed that such an approach can be used to achieve higher filler contents while maintaining strength properties. One of the side-benefits of such an approach is that the system becomes less dependent on subsequent addition of a retention aid to retain filler. Backing off on the amount of retention aid can make the paper somewhat more uniform, which also tends to contribute to higher strength.

The role of fines in helping to hold paper together, overcoming a strong debonding effect by fillers, was demonstrated in some carefully designed experiments by Xu *et al.* (2005). Pairs of filler-free, damp handsheets were prepared, and a sparse layer of filler particles was placed between them. Bonding agent was applied either to the handsheet surfaces or to the filler particles. After drying, the resistance to delamination was measured. Treatment of one or both plies with the bonding agent was found to increase bonding between the sheets, but that approach was effective only below a critical level of filler addition between the plies. Treatment of the PCC helped bonding to a modest degree, without as sharp a fall-off in properties when the filler loading between the plies was increased. But the highest strength in systems containing a lot of PCC between the plies was observed when cellulosic fines were present together with the PCC between the plies. The fibrillar fines created by refining were found to be much more effective in terms of bonding in such situations compared to the primary fines present in the pulp before refining (Xu and Pelton 2005).

Approaches involving treatment of the surfaces of filler particles with a bonding agent also might be considered in the "nano" category, given the very small thickness of such adsorbed layers. For instance, it has been shown that the cooking of starch in the presence of mineral particles can be a practical way to cover each particle with a thin layer (Yan *et al.* 2005; Zhao *et al.* 2005; Deng *et al.* 2010). Increased paper strength appears to be a key benefit of such an approach. In practice there is likely to be an overlap between treatments aimed at enhancing the bondability of filler particle surfaces and those aimed at agglomerating them together, as was discussed earlier.

One of the most effective, but difficult to achieve means of minimizing the adverse effect of mineral particles on paper strength properties involves loading them either into the lumens or cell walls of fibers, ideally leaving the fiber surfaces uncovered and available for bonding with adjacent fibers (Green *et al.* 1982; Middleton and Scallan 1985, 1989). Such approaches were reviewed recently by Kumar *et al.* (2011). Though lab results have shown potential to achieve superior strength properties at a given mineral content, there is little indication of successful implementation of such an approach at a commercial scale.

In a related approach, calcium carbonate particles can be precipitated in the presence of cellulosic fibers. Ciobanu and Bobu (2009) carried out such work and showed that the resulting optical properties of the paper exceeded what was achieved when conventional PCC was used. In addition, the filler remained firmly fixed on or in the fibers during a simulated recycling operation, thus minimizing the loss of materials. However, lower strength was observed compared to use of conventional fillers; such results suggest that the *in-situ* procedure, at least in the reported case, had a greater debonding effect.

If one's goal is to replace fibrous cellulosic material with something else, while maintaining a suitable structure in a paper product, it makes logical sense to consider fibrous mineral particles. For instance, certain calcium silicate minerals, composed of clusters of long fibrous elements, have shown promise for achieving high bulking, high optical characteristics, and favorable strength properties of the resulting paper (Mathur 2004). Some key challenges facing such approaches include health hazards associated with certain highly insoluble fibrous minerals (Sturm 2010), the huge difference in size between typical cellulosic fibers and typical mineral fillers (Bown 1983), and the high levels of abrasivity that would be expected if the size of typical mineral particles were to be increased greatly (Rapp and Laufmann 1995). Consistent with these constraints, Hu *et al.* (2009) and Chen *et al.* (2011) showed that favorable strength results can be obtained with the use of whisker-like $CaCO_3$ particles, which are sufficiently soluble so that significant health concerns do not seem to arise. Chen *et al.* (2011) suggested that the whiskers were partly embedded in the fiber walls, thus increasing a frictional contribution to paper strength.

Nanocellulose wet-end addition and paper strength

Much progress has been achieved in recent years to identify various promising ways of preparing nano-sized cellulosic materials, such as nanofibrillated cellulose and nanocrystalline cellulose. Such approaches have been reviewed (Klemm *et al.* 2011; Peng *et al.* 2011; Ramires and Dufresne 2011; Chauhan and Chakrabarti 2012). The cellulose nanomaterials themselves can be exceedingly strong (Saito *et al.* 2013). In addition, paper-like sheets formed from various 100% nanocellulose suspensions have achieved outstanding strength levels (Klemm *et al.* 2011), in addition to some unique features such as translucency (Iwamoto *et al.* 2005; Yano *et al.* 2005). Two challenging issues seem to be standing in the way of greater implementation of such approaches. The first issue is the relatively low yields of certain nanocellulose products. For instance, when cellulose nanocrystals are isolated from cotton, a relatively pure cellulose source, yields can be about 61% of the starting material (Pirani and Hashaikeh 2013). Notably, the cited authors were able to recover much of the material solubilized during preparation of nanocrystalline cellulose and reprecipitate it as potentially useful cellulose II. The second issue is energy. If cellulosic nanomaterials are prepared from kraft fibers, for instance, mainly by application of high levels of mechanical shearing, the energy input can be in the range 12,000 to 70,000 kWh/ton (Eriksen *et al.* 2008; Klemm *et al.* 2011). Based on these considerations, the present review article will not further consider the possibility of making paper from high proportions of cellulosic nanomaterials.

The question of whether nanocellulose could contribute to paper strength when used as a wet-end additive has been considered by several groups. Ahola *et al.* (2008) used nanofibrillated cellulose (NFC) together with a cationic wet-strength polymer, poly(amidoamine epichlorohydrin). By adding the polyelectrolyte first, a dense layer of NFC could then be layered onto the fibers. By contrast, pre-mixing of the polyelectrolyte and NFC gave rise to agglomerates, which tended to form less uniform and more rigid layers when added to the fiber slurry. Increases in both wet- and dry-strength properties were observed, especially when the additives were applied sequentially to the fiber slurry.

Related work was reported more recently by Joseleau *et al.* (2012), who compared the effects of once-dried cellulosic fines (*i.e.* “dead fines”) in comparison to what they called microfibrillar cellulose, freshly created by refining. The freshly prepared fines were found to generate 30% more hydrogen bonding within the sheet, according to a test using 6 M urea solution. The authors assumed that the urea would selectively detach those cellulosic fines that were attached to fibers by hydrogen bonding. Eriksen *et al.* (2008) showed that nanofibrillated cellulose could increase the tensile index of sheets made from thermomechanical pulp. Guimond *et al.* (2010) observed increased tensile strength when cellulose nanofibers produced by TEMPO oxidation were added to a newsprint grade furnish. Gao *et al*. (2011) showed that bacterial cellulose, added in small proportions, was able to increase the strength of sheets made from softwood fibers. González *et al.* (2012) showed that nanofibrillated cellulose (NFC) can be used as a kind of substitute for refining of the fibers themselves; combining the NFC with unrefined *Eucalyptus* kraft fibers gave about the same effect as refining of the fibers. Dai and Fan (2013) modified the surface of hemp fibers by high-pH treatment with cationic surfactant and nanocrystalline cellulose. As confirmed by various analyses, such treatment increased the strength of the fibers themselves, filling in the gaps in the cell wall and between fibrils.

Taipale *et al.* (2010) found that several different forms of nanocellulose were able to increase paper strength, and most such systems tended to slow the rate of drainage.

Fortunately, it appears that the adverse effects on dewatering can be overcome by careful selection of materials and process conditions. There is a critical need for research aimed at maximizing both dry strength and dewatering when adding nanocellulose products at the wet end. Presumably it might be beneficial to precipitate the nanocellulose onto fiber surfaces, where it might play a role analogous to that of surface-bound cellulosic fibrils rather than as detached cellulosic fines.

Nanomaterials use in paper coatings

Nanomaterials having a high aspect ratio, such as fibrillar nanocellulose or highly platy clay-like particles, have potential to increase the elastic modulus of coating layers, thus increasing the stiffness of paper products. In such applications the reinforcing role of the nanocellulose can be understood in terms of nanocomposite technology, which has been discussed in earlier review articles (Hubbe *et al.* 2008b; Siro and Plackett 2010; Kalia *et al.* 2011; Moon *et al.* 2011; Johansson *et al.* 2012; Khalil *et al.* 2012). Cengiz (2001) observed increased strength upon introduction of nanoparticles to a mixed resin applied to paper. Husband *et al.* (2009) were able to achieve higher stiffness by incorporating a highly platy fine clay into coating layers on paper. Despite such evidence of potential contributions to stiffness, such approaches face inherent challenges. In particular, many coated grades of paper have challenging targets of gloss and print quality, which are likely to be more difficult to meet when incorporating high-aspect-ratio nanomaterials. Also, the high-shear flow characteristics of the coating formulation can be adversely affected when high aspect ratio materials are used (Lohmander and Rigdahl 2000; Willoughby and Sharma 2004; Kugge *et al.* 2011). Paunonen (2013) has reviewed progress related to the use of nanomaterials in laminate films on paper products, for the enhancement of both strength and barrier properties.

Chemical Strategies for Stronger Bonding

Though some fibers break during the tensile failure of a paper structure, most of the damage often involves failure of inter-fiber bonds (Van den Akker *et al.* 1958; Page 1969a). This section will consider chemical strategies that could be used to make such bonds stronger.

Alkaline processing

One of the most remarkable features of papermaking technology is the fact that quite strong bonding can be achieved among the fibers even without adding any type of glue. Thus, it is appropriate first to consider what can be done to strengthen paper just by more effective swelling of the fibers. Several studies have shown that one of the most effective ways of accomplishing this objective is by use of alkaline pH conditions (Young 1994). For instance, the following studies showed that alkaline conditions used in the repulping of fibers then can promote easier swelling during refining, thus leading to higher strength (Szwarcsztajn and Pryzybysz 1976; Klungness and Caulfield 1982; Guest and Voss 1983; Bhat 1991; Gurnagul 1995; Ogden 1999). Pönni *et al.* (2013) found evidence that alkaline conditions can re-open pore surfaces within fibers that previously had been closed due to drying. Gurnagul observed benefits from alkaline processing of recycled fibers in the case of thermomechanical pulp (TMP); no such benefits were observed when similar treatments were applied to low-yield recycled fibers. Such results are consistent with the effect of carboxyl groups on the swelling of pulps under different pH conditions (Lindström and Carlsson 1982; Lindström and Kolman

1982). Other studies have shown a similar positive effect associated with weakly alkaline conditions employed during the formation of paper (Lindström and Kolman 1982; Forester 1985). An added benefit of such processing conditions is that the fibers within paper formed under neutral or weakly alkaline pH conditions are then less subject to acid hydrolysis during storage of the paper (Williams 1980; McComb and Williams 1981; Scallan 1998; Weise 1998).

Application strategies for dry-strength additives

Gruber *et al.* (1996) carried out an interesting thought experiment by considering all of the different kinds of additives, as well as fibers, cellulosic fines, and mineral particles, in a typical papermaking operation. On this basis they estimated that about 100 different pair-wise interactions can be expected to be important during papermaking. To begin to make sense of the complexity, it was recommended to focus on processes of adsorption, noting that the sequences of addition can affect how the additives perform in a paper machine system. Rojas and Neuman (1999) observed unique adsorption phenomena in systems that contained both charged and uncharged hydrophilic species; it appeared that adsorption of polysaccharides onto fibers resulted in the complexation of some other species. To explain their findings the cited authors needed to go beyond the usual explanations based on electrostatic charges. Factors such as hydrogen bonding, hydrophobic effects, and the entropy changes that occur upon adsorption in different situations appear to be important. These various levels of complexity, even in a highly conventional paper machine system, can help to explain the patient trial-and-error approach that paper machine operators face in their day-to-day work.

Conventional wet-end strategies are often classified using such terms as single- or dual-additive programs. Many single-polymer wet-end treatments have shown promise for dry-strength development. For instance, Retulainen and Nieminen (1996) compared a range of different polymeric additives on a one-at-a-time basis and found that the cationic starch products had the greatest beneficial effects on paper strength. Decreases in strength were observed in the cited study when using polyelectrolytes having a sufficiently high molecular weight to cause strong flocculation of the fibers. In line with this observation, various studies have suggested that there can be an optimum range of molecular weight of dry-strength agents, depending also on such factors as linear *vs.* branched molecular structure (Reynolds and Wasser 1980; Hubbe 2006). In addition, some studies have provided evidence that dry-strength agents based on natural gums (Swanson 1950; Leech 1954) or acrylamide (Carlsson *et al.* 1977) can outperform typical starch-based products due to favorable properties of the chemical structure.

Cationically charged dry-strength additives often have been found to have greater effectiveness than their uncharged or anionic counterparts when added to papermaking furnish in the absence of other cationic materials. Such results often can be attributed to more efficient retention on fibers during the papermaking process (Roberts *et al.* 1986, 1987). Horvath *et al.* (2008) showed that cationic polyelectrolytes having a sufficiently high density of change tend to remain immobilized near to their first points of contact with a negatively charged material. Such behavior can, in principle, have a favorable effect of keeping a cationic additive at the fiber surface and thereby able to contribute to bonding.

Still focusing on approaches that can be considered as well-established in the industry, certain "dual additive" systems can be used in efforts to push bonding strength somewhat beyond what can be achieved by cationic starch addition to the same furnish.

For instance, sequential addition of a relatively high-charge cationic polymer, together with a carboxylated (anionic) polymer, *i.e.* a dual system, has been shown to be highly effective for increasing dry strength (Linke 1968; Hubbe *et al.* 2003; Wielema and Brouwer 2003; Esser *et al.* 2005; Galván *et al.* 2012). As shown by Hubbe *et al.* (2003), it can be an effective strategy to add just enough of the cationic additive, in the first step, so that the fiber surfaces are saturated; subsequent addition of the anionic component of the dry-strength system was found to be especially effective. This strategy is illustrated in Fig. 9. Somewhat higher dry strength levels, compared with single-polymer dry-strength strategies, were attributed to higher amounts of retained bonding agent, as well as a more three-dimensional extension of polymer segments from the fiber surfaces prior to bond formation.

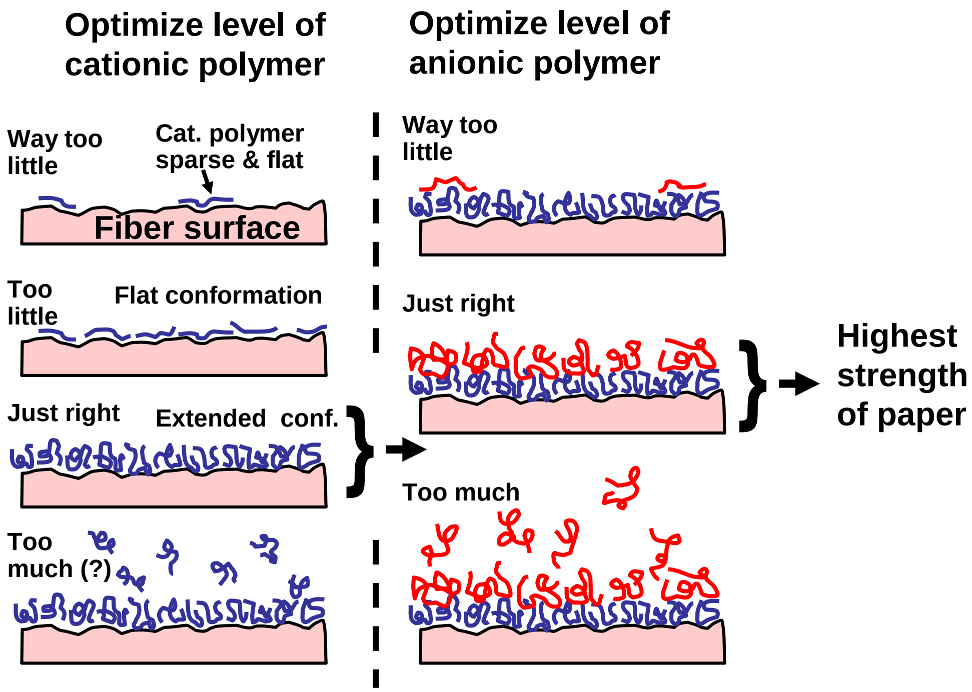

Fig. 9. Illustration of dual-polymer dry-strength additive strategy based on saturation of adsorption capacity of the fibers, thus achieving a more extended conformation and higher levels of adsorbed polymers

Initiatives to supplement the hemicellulose content of fibers

As was noted earlier, vigorous pre-extraction of wood chips has been suggested as a way to reduce costs associated with pulping and bleaching, but the resulting pulp can be deficient with respect to bonding ability (Oksanen *et al.* 1997; Al-Dajani and Tschirner 2008; Yoon and van Heiningen 2008). Thus, it makes sense to consider what would happen if hemicellulose, either in its extracted form or after modifications, were added to kraft pulp fibers – whether or not those fibers had been subjected to pre-extraction. In general, studies have shown that addition of hemicellulose products to the fiber slurry tends to increase the strength of the resulting paper (Mobarak *et al.* 1973; Bhaduri *et al.* 1995; Denis *et al.* 2003; Lima *et al.* 2003; Suurnäkki *et al.* 2003; Ahrenstedt *et al.* 2008; Zhang and Hu 2010; Han *et al.* 2012; Bigand *et al.* 2013; Lindqvist *et al.* 2013; Song and Hubbe 2013, 2014). Lima *et al.* (2003) reported steeply rising dry strength upon addition of unmodified seed-derived xyloglucan to eucalyptus kraft fibers as the dosage was increased in the range zero to about 1% in the absence of any retention aid. Higher amounts provided little additional effect, suggesting that 1% was the adsorption capacity of the pulp. The fact that the resistance to air penetration also rose sharply indicated that the hemicellulose promoted densification of the paper. Bai *et al.* (2012) compared wet-end addition of three different hemicellulose types and found that galactoglucomannan had the largest beneficial effect on strength, followed by xylan and arabinogalactan.

Derivatizing hemicellulose to provide it with a positive charge has been shown to increase its effectiveness as a wet-end dry-strength additive (Ren *et al.* 2009, 2011; Liu *et al.* 2011a; Schwikal *et al.* 2011; Kataja-aho *et al.* 2012; Bigand *et al.* 2013), presumably due to the better retention on the fiber surfaces. Schwikal *et al.* (2011) observed an optimum in strength performance at an intermediate level of cationic charge density. Lindqvist *et al.* (2013) found that the effects of galactoglucomannans as dry-strength agents could be improved in various aspects by carboxymethylation, cationization, or partial hydrophobation. Likewise, Song and Hubbe (2013, 2014) showed that increasing the amount of carboxyl groups in glucan obtained from oats by TEMPO-mediated oxidation or by carboxymethylation greatly increased its effectiveness as a dry-strength agent when used in combination with aluminum sulphate and a cationic retention aid. The higher strength results were attributed to higher solubility of the modified glucans, leading to their better distribution in the furnish.

It has sometimes been assumed in the past that addition of hemicellulose during the cooking of kraft pulps would be a waste of resources due to the likelihood of molecular breakdown or dissolution during subsequent bleaching and washing operations. However, Danielsson and Lindström (2005) observed a significant increase in tensile strength upon addition of a high-mass xylan to a softwood kraft cook. The central importance of the bonding contribution of the xylan was supported by the fact that high-mass xylan had a much greater beneficial effect than low-mass xylan. The ability of hemicellulose to remain on fiber surfaces and to withstand pulping and bleaching operations is not well understood.

Another option to consider is the addition of hemicellulose to fiber stock before refining of the fibers (Lima *et al.* 2003; Han *et al.* 2012). Such practices are consistent with the traditional use of "beater adhesives," especially in the years before development of cationic wet-strength agents capable of adsorbing efficiently on the fiber surfaces (Swanson 1950). Addition of uncharged polysaccharides and other additives before the refiners not only gave the additives more time to become adsorbed on the fibers, but also such treatment was found to accelerate the reduction in freeness values during refining (Walecka 1956; Centola and Borruso 1958; Becka 1979; Allan *et al.* 1985; Blomstedt *et al.* 2007). In each case the mechanism appears to involve an increase in the negative charge density of the surface, following adsorption of the respective additive. Accordingly, Walecka (1956) observed more rapid decreases of freeness during refining with increasing degree of substitution of carboxymethylcellulose (CMC). The higher charge of the cellulosic material, after adsorption of the negatively charged additive, results in a higher degree of swelling, leading to more effective development of bonded area and a higher density of hydrogen bonds connecting the fibers after drying. In the work of Lima *et al.* (2003), though addition of seed-derived hemicellulose to eucalyptus kraft pulp at the 1% level before refining appeared to increase bonding strength, somewhat greater increases were observed when the addition was made after refining.

Treatment of papermaking fibers with carboxymethylcellulose (CMC)

Despite the fact that it has a strong negative charge, which is the same sign of charge as untreated cellulosic fibers, a series of studies have shown that CMC can be successfully deposited onto fiber surface, and strong increases in dry strength have been observed in the resulting paper (Walecka 1956; Laine *et al.* 2002, 2003a,c; Watanabe *et al.* 2004; Duker and Lindström 2008; Aarne *et al.* 2012a). The cited studies have considered, among other things, why the reported treatments of fibers with CMC appear to be quite effective, even when no cationic additive has been employed. By contrast, earlier users employed cationic additives such as alum to retain CMC to develop dry strength (Horsey 1947). Subsequently it has been shown that addition of calcium chloride or other salts can facilitate the adsorption of the anionic CMC onto generally anionic cellulosic surfaces (Laine *et al.* 2002; Duker and Lindström 2008; Liu *et al.* 2011b). Evidence of a special affinity between CMC and pure cellulose surfaces was shown by Kargl *et al.* (2012), who attributed the favorable adsorption to chemical similarity. It was suggested by Laine *et al.* (2000) that the effect can be attributed to a form of co-crystallization between the flexible CMC macromolecules and the partially crystalline cellulose surfaces to which they are adsorbed. Such an explanation is consistent with the relatively long treatment times that have been found necessary in the cited studies to achieve the best results; such a conclusion follows from the idea that substantial time may be required for fairly long CMC molecules to become well lined up with the adjacent cellulose chains, rather than remaining adsorbed in a disorganized and presumably less stable fashion.

The adsorption of CMC will provide the cellulosic surface with a much greater negative charge density, thus leading to greater swelling. An unfavorable aspect of such procedures, in addition to the cost of the CMC, is the requirement that salts ordinarily need to be added to suppress electrostatic repulsions sufficiently to allow the adsorption of CMC to proceed (Laine *et al.* 2000). Such salts, upon release of effluent from the process, would be expected to adversely affect fresh water organisms (Canedo-Arguelles *et al.* 2013). To some extent this problem can be minimized by using CMC having a relatively low degree of substitution, thus lowering its solubility in water and minimizing the concentration of salt needed to encourage its adsorption from solution onto the fibers (Watanabe *et al.* 2004).

Carboxylation of fiber surfaces

As a possible alternative to the adsorption of CMC, as just described, some researchers have considered oxidation or derivatization of fiber surfaces to increase their negative charge density. Such chemical derivatization of fiber surfaces can be viewed as a relatively aggressive strategy, compared to relying on adsorption. Carboxylation, leading to higher bonding strength in paper, has been achieved by periodate oxidation (Alince 1975), by carboxymethylation (Ruffini 1966; Lindström and Carlsson 1982; Laine *et al.* 2003; Torgnysdøtter and Wågberg 2003), by ozone treatment (Minor *et al.* 1993), by TEMPO-mediated oxidation (Kitaoka *et al.* 1999; Le Roux *et al.* 2006; Song and Law 2010; Aracri *et al.* 2012; Ma *et al.* 2012), or by enzyme-catalyzed derivatization with various carboxylic acid or aldehyde-containing species (Liu *et al.* 2013). Most of the cited studies showed increased strength of paper prepared from the modified fibers.

In the dry state, fibers can be oxidized by corona treatment (Goring and Suranyi 1969; Cramm and Bibee 1982) or by exposure to the vapors of maleic anhydride (Hubbe *et al.* 1999), with similar positive effects on paper strength after reslurrying those fibers.

All of these effects are consistent with increased swelling of the fibers with increasing amounts of anionic charge. The more swollen fibers can be expected to undergo more effective integration of cellulosic surfaces at the nano-scale during the drying process. The effect also is consistent with a model in which hydrogels, when dried in contact with each other, become fused together due to some mixing of polymeric chains in a three-dimensional transition zone at what used to be the interface (Pelton 2004).

Three-dimensional extension of adsorbed dry-strength agents

Many studies considered in an earlier review article (Hubbe 2006), as well as some more recent studies (Fatehi *et al.* 2010; Bai *et al.* 2012; Kataja-aho *et al.* 2012) have shown that the performance of various dry-strength enhancing polymers increases with their molecular mass. There are at least two explanations for this trend. On the one hand, a higher-mass polymer in solution will require more time to diffuse into the mesopores of fiber and thus lose its function as a bonding agent (Wu *et al.* 2009). On the other hand, a higher-mass polyelectrolyte adsorbed at a surface can be expected to spend more time in an extended, three-dimensional conformation before it is able to flatten itself out on the surface (Wågberg *et al.* 1988, 1996). During the seconds or minutes that the adsorbed hydrophilic polymers remain in an extended conformation, one can expect there to be more effective development of bonding with a second fiber, as paper is being formed. Such a mechanism is supported by observations that, in very clean pulp systems, low-density cationic polymer strength additives often out-perform higher charge-density additives (Fatehi and Xiao 2008). A loopy structure is expected in such cases because uncharged, hydrophilic segments of a polymer chain can be expected to extend away from the surface.

Layer-by-layer (polyelectrolyte multilayer) technology

Some remarkable and sometimes idiosyncratic increases in paper strength have been achieved in various recent studies that have employed “layer-by-layer” or “polyelectrolyte multilayer” (PEM) technology. In principle, PEMs are built up by first dipping the substrate into a solution containing a polyelectrolyte having an opposite sign of charge from that of the substrate. Then the substrate is dipped into a rinsing solution, often followed by a drying step. Then the process is repeated, starting with a bath containing polyelectrolyte of the opposite charge. The process is continued back and forth, building up as many layers as the investigators have patience to apply. The majority of studies aiming to understand the science underlying PEM effects have involved the use of very smooth surfaces, such as mica or quartz crystals (Decher 1997). Such surfaces have made it possible to precisely quantify the changes in layer thickness and new adsorbed amount with each additional cycle of layering. Best results, in terms of layer regularity and adsorbed amounts, typically have been achieved in systems containing a salt concentration that has been optimized so as to suppress the range of electrostatic forces and allow the polyelectrolytes to adsorb in a coiled, rather dense conformation.

Though it is often not practical to replicate all aspects of the usual PEM approach when using cellulosic fibers (such as drying the substrate after each application of a layer or precisely measuring the layer thicknesses), several such studies have been carried out (Wågberg *et al.* 2002; Eriksson *et al.* 2005a,b, 2006; Torgnysdøtter and Wågberg 2006; Brännvall *et al.* 2007; Lingström and Wågberg 2008; Ankerfors *et al.* 2009, 2012; Zhou *et al.* 2010; Chin *et al.* 2012; Li *et al.* 2012a). Polyelectrolyte bilayer application based on the same principles, and its effect on paper strength, also has been reported (Myllytie *et al.* 2009; Aarne *et al.* 2012a). To summarize what is most often observed in such studies, paper's dry strength has been found to increase with increasing numbers of polyelectrolyte bilayers. In certain cases, higher strength has been observed when a certain one of a pair of polyelectrolytes is outermost (Wågberg *et al.* 2002; Eriksson *et al.* 2005b). Eriksson *et al.* (2005a) showed that accelerated deposition of increasing amounts of polyelectrolyte during successive cycles could be achieved by switching the pH conditions back and forth such that the charge of the outermost already-adsorbed layer was much greater than an equal amount of the next-to-be adsorbed layer.

Aarne *et al.* (2012a) found that they were able to achieve a favorable combination of relatively low water retention value (WRV) and strong positive contribution to dry strength when adding enough high-charge cationic polymer to approximately neutralize the net charge of fibers that had been coated with an initial layer of the anionic CMC. Such a result was unexpected, since increased swelling of papermaking fibers is usually associated with development of higher bonding strength. The strengthening effect also was able to be carried over efficiently to recycled sheets, obtained under relatively gentle laboratory conditions.

Cranston and Gray (2009) have reviewed studies in which nanocellulose was applied as one of the layers in PEM strategies. For instance, Ahola *et al.* (2008) employed a system in which cellulose nanofibrils constituted one of the layers, added after a layer of cationic polyamidoamine-epichlorohydrin wet-strength polymer; a bilayer addition strategy was found to increase both dry-strength and wet-strength. Aulin *et al.* (2010) incorporated the alternating use of two types of treated nanocellulose into a layer-by-layer strategy. Microfibrillated cellulose batches were prepared with either cationic or anionic surface charge.

Polyelectrolyte complexes for dry strength

If one mixes together solutions of polyelectrolytes having opposite charges, the mixed polymeric material is likely to become decreased in solubility, often precipitating out of solution (Michaels 1965). Several studies have employed the principles of polyelectrolyte complexation as a means of treating cellulosic fiber surfaces with relatively high amounts of hydrophilic polyelectrolyte material, thus enhancing paper's dry strength (Carr *et al.* 1974, 1977; Heath *et al.* 1974; Nagata 1991; Gärdlund *et al.* 2003, 2005; Gernandt *et al.* 2003; Koljonen *et al.* 2003; Hubbe 2005a; Hubbe *et al.* 2005; Lofton *et al.* 2005; Maximova *et al.* 2005; Heermann *et al.* 2006; Lvov *et al.* 2006; Torgnysdøtter and Wågberg 2006; Truppner *et al.* 2006; Vainio *et al.* 2006; Larsson and Wågberg 2008; Ankerfors *et al.* 2009, 2012; Fatehhi *et al.* 2009; Sang *et al.* 2010). As noted by Rojas and Neuman (1999), even in papermaking systems where there has been no explicit intention to form polyelectrolyte complexes (PECs), such effects still can play a role due to interaction between a cationic polyelectrolyte and various anionic polyelectrolytes already present in the suspension, such as dissolved hemicellulose species.

Effective complexation of polyelectrolytes, leading to increases in paper strength, do not necessarily require that both additives are polyelectrolytes. Thus, highly promising results have been achieved by sequential addition of anionic wet-end starch with an aluminum-based coagulant (Brouwer 1997; Wielema and Brouwer 2003). Also it is likely that some reports of favorable dry-strength improvements obtained with mixtures of native starches and cationic polymers might be due to formation of PECs (Wu *et al.* 2004), especially if the native starch has some anionic character. Similarly, Bhardwaj *et al.* (1997) achieved promising improvements in dry strength upon addition of a combination of amphoteric starch and cationic acrylamide copolymer.

Though most of the studies cited in the preceding paragraph have involved pre-mixing of pairs of polyelectrolyte solutions before their addition to papermaking furnish, such a strategy had been shown to give less favorable effects on paper's strength in comparison to *in-situ* addition, *i.e.* allowing the two polyelectrolyte solutions to come into contact in the presence of a stirred fiber suspension. For instance, Hubbe (2005a) reported that *in-situ* formation of PECs was able to achieve roughly twice the tensile strength compared to addition of pre-formed PECs of the same composition to a suspension of otherwise non-bonding glass microfibers. As shown in Fig. 10, the best results were achieved when the ratio of additives was within a range of 40:60 to 60:40 relative to the charge stoichiometry of the two polyelectrolytes employed. Tensile breaking force continued to rise to higher and higher levels even when the level of polymer addition was pushed to startlingly high levels, up to 10% of the total mass of solids in the resulting paper sheet. The lowest strength was observed if, after premixing the two polyelectrolytes with each other, the addition of the PEC mixture to the fiber suspension was delayed by several minutes.

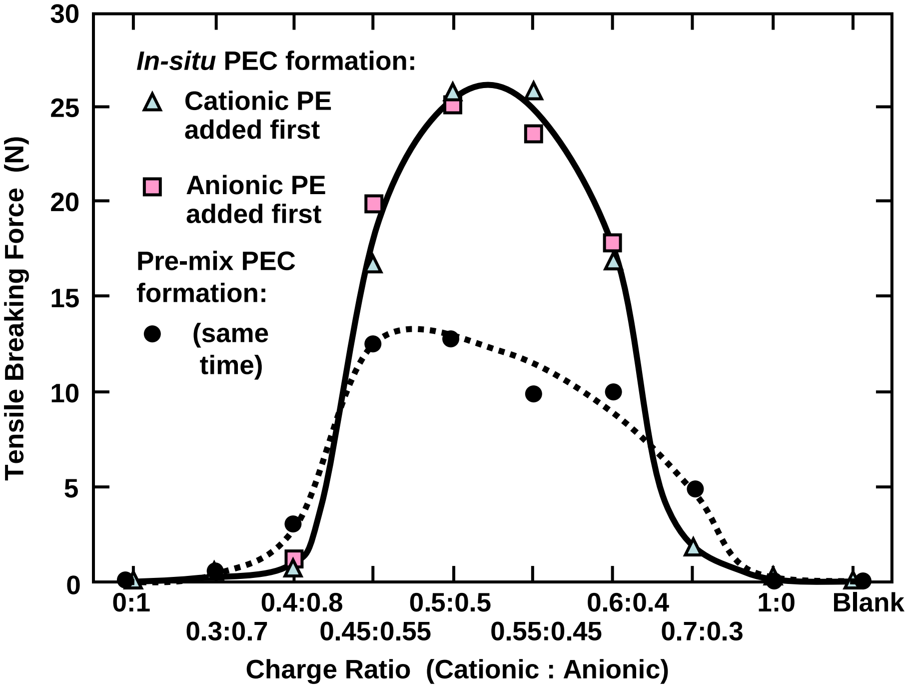

Fig. 10. Replotting of data from Hubbe (2005a) in linear form to highlight strong advantage of *in-situ* PEC formation to achieve high tensile strength when using glass microfibers that do not bond together on their own or even with single polyelectrolytes

In follow-up work involving typical kraft pulp fibers, Heerman *et al.* (2006) showed that it was possible to push net polyelectrolyte addition levels up to unheard-of levels as high as 40% of the weight of fiber, again with sharply rising dry strength with increasing polymer dosage. At such high levels of polyelectrolyte addition, the product might reasonably be classified as a composite rather than as ordinary paper. By employing the *in-situ* addition method it was possible to delay the onset of serious problems related to stickiness by a factor of about ten in the net amount of added polymer. Again it was shown that much higher tensile strength values could be achieved by the *in-situ* addition scheme, in comparison to pre-mixing of the polyelectrolytes. Such high levels of treatment seem unlikely to be implemented commercially, partly due to the generally higher costs of polyelectrolytes in comparison to the fibers. However, it is clear that the use of PECs offers a way to achieve dry strength levels that greatly exceed what can be achieved by adsorption of a single polyelectrolyte.

The ratio between the positively and negatively charged polyelectrolytes was found to play a critical role in the PEC systems just described (Hubbe 2005a,b). In general, when the fibers in suspension had a negative surface charge, somewhat higher adsorbed amounts of polyelectrolyte, as well as higher dry strength, were obtained when the PEC mixture was either charge-balanced or as a 55:45 ratio of cationic to anionic polymer-bound ionic groups.

To attempt to explain the much greater effectiveness of *in-situ* formation of PECs, by balanced sequential addition of polyelectrolytes of opposite charge to a stirred suspension of fibers under moderately low electrical conductivity conditions, it is apparent that kinetic effects are important. It is proposed, therefore, that the freshly-formed PECs are in some sense “active” and able to interact with the fibrils and other surfaces of cellulosic fibers in ways that are no longer effective if the PECs are formed separately and added later. For instance, it is reasonable to expect progressive dehydration and densification of PECs with the passage of time after their preparation. The word “self-assembly” has sometimes been used to denote processes in which events occur at the nano scale, based on the nature of the materials and the interactive forces. Further research work is needed, perhaps with molecular dynamics simulation or quartz crystal microbalance (QCM) measurements, to shed more light on such mechanisms. Another issue that might be explored in future work is whether polyelectrolyte complexes might contribute to more flexible and resilient attachments between fibers in the wet web; such flexibility could lead to more effective sharing of the tensile loads once the paper has been dried.

Microparticle systems as an example of polyelectrolyte complexes

A type of polyelectrolyte complexation also appears to underly the widespread application, within the paper industry, of cationic polyelectrolytes in sequential addition with negatively charged colloidal solids such as colloidal silica, montmorillonite (bentonite), and certain hydrogel products (Swerin *et al.* 1995; Wågberg *et al.* 1996; Hubbe 2005b; Khosravani *et al.* 2010; Kim and Hubbe 2010). Some similarities with conventional polyelectrolyte complexation can be noted. For instance, in both cases a balance between positive and negative charges tends to minimize the amount of water held within the structure and to favor precipitation of the material out of solution and onto the surfaces of fibers. For that reason, microparticle systems can be viewed not only as a strategy to optimize retention and dewatering, but also as a way to more effectively retain a dry-strength additive, such as cationic starch. Indeed, various studies have shown that combinations of cationic starch and colloidal silica can be beneficial for increasing paper’s dry-strength properties (Moberg 1985, 1986; Nilsson and Carlson 1993; Sunley 1997; Khosravani and Rahmaninia 2013).

As shown in Fig. 11, it is possible to envision microparticle systems as being a type of nanocomposite, in which fused chains of nano-sized silica particles serve as reinforcement within a matrix composed of cationic starch. The colloidal silica can be expected to play two key roles. First, by having a large surface area and strongly negative surface charge, it neutralizes the positive charge of the starch, thus promoting the deposition of the starch on the fiber surfaces. Secondly, one can expect that the silica renders the combined adhesive material more rigid once the starch-silica mixture has been dried.

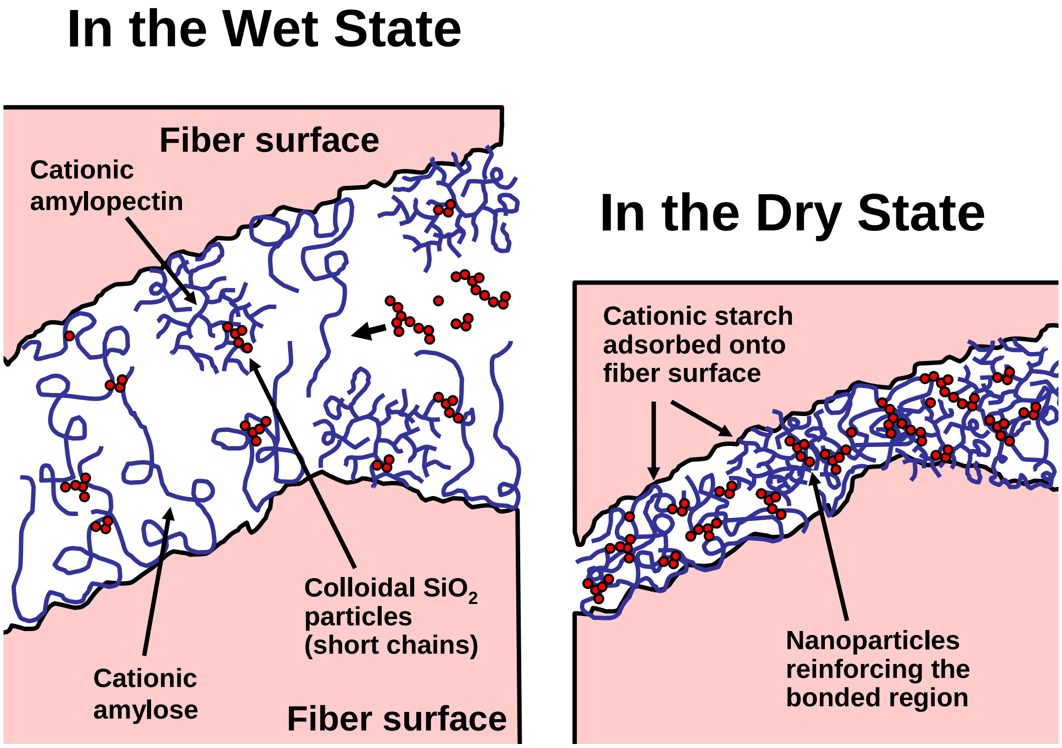

Fig. 11. Illustration of the role of chain-like colloidal silica particles within a matrix of cationic starch, serving as reinforcement in a resulting “nanocomposite” adhesive between fibers in paper

Silva *et al.* (2013) reported another promising approach in which cellulose nanocrystals were employed, together with cationic starch, as the anionic component of a PEC system. The greatest increases in paper dry strength were obtained under conditions of balanced charges between the starch and the nanocellulose. A unique and promising aspect of this kind of approach is that nanocellulose particles typically are highly fibrillar, and thus in principle able to provide structural reinforcement to bonded areas. More research is needed in order to figure out how both the macro-scale structures and the nano-scale structures within paper can be optimized simultaneously by control of additives and process conditions during papermaking. Otherwise, due to such factors as shrinkage during drying, one can imagine the paper structure developing gaps and non-uniformities, leading to lower than the anticipated levels of strength.

Polyampholytes as dry-strength agents

The terms “polyampholyte” and “amphoteric polymer” refer to polyelectrolytes that have both cationic and anionic substituent groups. Several studies have shown that polyampholytes sometimes outperform otherwise similar dry-strength additives having only one sign of charge (Fukunaga 1999; Song *et al.* 2006, 2010; Wang *et al.* 2006, 2007b; Hubbe *et al.* 2007a,b; Silva *et al.* 2009). Relative to polyelectrolytes bearing a single sign of charge, polyampholytes offer two important potential advantages: On the one hand, they are not expected to cause strong flocculation of a fiber suspension. This expectation was borne out in tests measuring the state of flocculation in suspensions of bleached kraft fibers (Hubbe *et al.* 2007a). On the other hand, because polyampholytes already can contain a balanced proportion of positive and negative charges, there is little risk that their addition to a paper machine system – even at rather high levels – will cause disturbances in the balance of charges in the system.

A series of tests were carried out to determine the effects of different charge-related quantities on the performance of polyampholytes as dry-strength agents. Terpolymers of acrylamide, itaconic acid (a monomer with two carboxylic acid groups and acrylamide), and a cationic monomer dimethylaminepropylacrylamide were prepared by random free-radical polymerization (Sezaki *et al.* 2006a; Hubbe *et al.* 2007a). Best results, in terms of dry strength, were obtained when the pH was adjusted so as to decrease the solubility of the polymer, favoring the precipitation of bonding agent onto the fibers (Fig. 12).

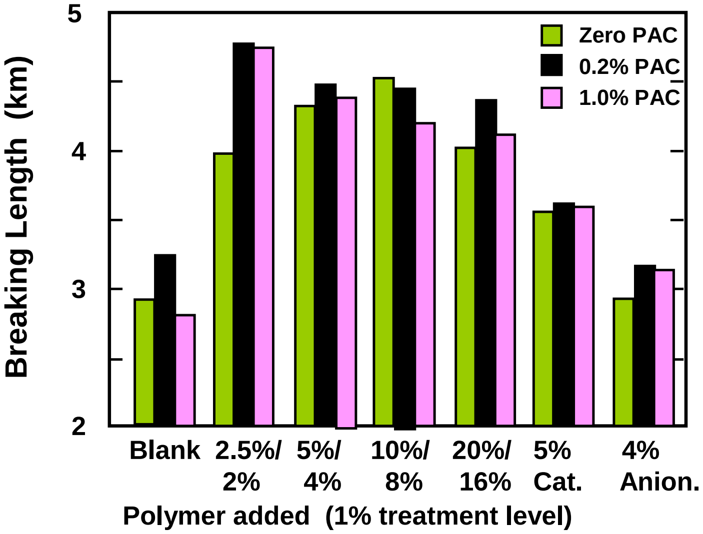

Fig. 12. Tensile strength resulting from addition of acrylamide-based polyampholytes having 5:4 charge ratio (cationic to anionic) at the 1% level to bleached kraft pulp at pH=5, followed by addition of the indicated amounts of poly-(aluminum chloride) (PAC) based on solids. The last two sets of three bars correspond to polyelectrolytes having a single sign of charge. Figure redrawn from Song *et al.* 2006.

Further work by Sezaki *et al.* (2006b) showed that adsorption of the polyampholytes onto cellulosic fibers tended to be maximized under conditions where the net charge was somewhat to the positive side of neutralization. Such a maximum was explained by the fact that it allows the polyampholyte to have a net charge opposite to that of the fiber surfaces, while at the same time to be sufficiently charge-neutralized so as to promote its relative insolubility in water and deposition onto the fibers. Follow-up tests with polyampholytes having a fixed charge ratio (5 parts cationic charge and 4 parts of anionic charge) showed high adsorption efficiency onto cellulosic fibers within a pH range of about 4 to 9 (Wang *et al.* 2006). High adsorption efficiency was observed over a wide range of the content of charged groups at the same fixed ratio, though there was notably lower adsorption efficiency at the lowest net charge considered (2.5% cationic charge and 2% anionic charge groups). As shown in Fig. 12, polyampholytes greatly outperformed the corresponding polyelectrolytes having only a single sign of charge (Hubbe *et al.* 2007a).

To explain the sometimes higher performance of polyampholyte systems, it might be assumed that the many ionic groups contained within such molecular chains have the ability to hold onto water, thus providing the molecules with a three-dimensional structure and the capability of participating in effective bonding between the rough surfaces of adjacent fibers. Such a model was supported by the results of water retention value (WRV) tests (Hubbe *et al.* 2007b). Related effects were also found by tests with the quartz crystal microbalance (QCM) method (Song *et al.* 2010). The QCM results showed that adsorption of polyampholytes resulted in a relatively large uptake of mass onto a model substrate, consistent with binding of water, along with the polymer adsorption. In addition, the observed changes in energy dissipation during the adsorption process revealed a non-rigid structure of the adsorbed material, which is consistent with a swollen, three-dimensional state of adsorption as a hydrogel within the time scale of the experiments.

Ionic bonding

A common feature of most of the dry-strength strategies discussed above is that ionic charges often play a central role. It is reasonable then to consider whether or not ionic bonds might make a significant contribution to adhesion between fibers in the paper after it has been dried. Though ionic bonds generally lack the water-resistance that is characteristic of most covalent bonds, their energy content can be large, in the range of about 90 to 180 kcal/mole to separate various pairs of oppositely charged univalent ions (Huheey 1972). This can be compared to a range of about 50 to 125 kcal/mole for typical covalent single bonds (Nebergall *et al.* 1980). This is much greater also than the energy associated with hydrogen bonds, which have been estimated as up to 20 kcal/mole in the case of cellulose (Nissan *et al.* 1985). Accordingly, it has been proposed that ionic bonds can play a significant role in the bonding of paper, depending on the chemical treatments (Allan and Reif 1971; Reif 1972).

Experimental evidence supporting ionic bonding has been hard to come by, possibly due to the possibility of multiple contributions to bond strength in typical cases. For example, zwitterionic groups in an acrylamide resin used to impregnate paper contributed a wet-strengthening effect to the paper (Delgado *et al.* 2004); however it is likely that much of the strength benefit was due to a more thoroughly entangled polymer structure brought about by the charge interactions – rather than an effect due to the ionic charges themselves. Likewise, one might argue that the demonstrated strength of adhesion within a polyelectrolyte multilayer (PEM) in the wet condition (Aulin *et al.* 2010) constitutes evidence of the importance of ionic bonding.

A problem with such evidence is that opposite charges can induce changes in flocculation, causing significant differences in the uniformity of paper (Delgado-Fornue *et al.* 2011). Torgnysdøtter and Wågberg (2004) measured the strength of adhesive joints formed between single fibers that were optionally treated to make the surface have a positive or negative charge. Increased strength was observed with increasing charge density of the fibers, an effect that might be related to ionic bonding; however, the results also could be explained by enhanced dewatering in a charge-balanced interaction, leading to a denser paper structure upon formation of the sheet. Allan and Reif (1971) avoided flocculation by preparing paper from fibers treated with strongly anionic CMC. Subsequent impregnation of the pre-formed sheets with the strongly cationic polymer polyethyleneimine (PEI) yielded very strong paper. One can envision the cationic PEI forming bridges between the negatively charged fiber surfaces already fully assembled in the sheet. Rojas *et al.* (2005) were able to avoid such complexities by measuring the adhesion between highly anionic mica sheets, one or both of which had been treated with cationic polymer. The strongest force, under wet conditions, was achieved in cases where just one surface had been treated with a high-charge-density cationic polymer – a situation consistent with a charge contribution to bond strength. However the observed bonding showed a highly reversible character – something more akin to adhesive tape, rather than the kind of adhesion that typically holds paper together. In addition to demonstrating the importance of ionic interactions in the cases considered, the study also demonstrated the importance of the viscoelastic nature of the cationic polyelectrolytes.

Aluminum as a strength booster

Since the early 1800s, aluminum-containing chemicals have been widely used by papermakers for such purposes as promoting retention of fine particles, increasing rates of drainage, and the setting of rosin size (Strazdins 1989; Kitaoka and Tanaka 2002). Investigations of the molecular mechanisms underlying such interactions have revealed a complex interplay between different soluble ionic species of hydroxylated aluminum species, along with a strong tendency towards the formation of oligomeric or polymerized species (Bottéro *et al.* 1980; Bi *et al.* 2004; Zhao *et al.* 2009). In that context it is perhaps not surprising that soluble aluminum species appear capable of boosting the dry-strength performance of polyelectrolytes in some hard-to-explain situations, such as when polyampholytes are used as dry-strength agents (Fukunaga 1999; Song *et al.* 2006). One possible way to explain such beneficial effects is to assume that complexation occurs between the high positive charge associated with oligomeric aluminum compounds and the negatively charged segments that can be expected to exist due to the random nature of synthesis of this type of amphoteric polymers. Then, upon the drying of the paper, one can expect the processes of polymerization and reorganization to proceed, such that an inorganic polymer structure at least partially interpenetrates the organic polymer. Such an interaction would be analogous to what happens when aluminum sulfate is added to the paper machine wet end in sequence with anionic dry-strength additives, serving to bond the latter to the negatively charged surfaces of fibers (Linke 1968; Wielema and Brouwer 2003).

Wet-end application of hydrogels, including uncooked starch

A hydrogel can be defined as a water-loving polymeric material that swells in aqueous solution but does not dissolve (or at least has not yet dissolved). The criterion that a promising candidate from dry-strength applications ought to be three-dimensional and highly swollen with water thus appears to be well fulfilled by materials in the hydrogel category. Some of the systems already discussed, such as polyelectrolyte multilayers and complexes, might be considered as being kinds of hydrogels.

Water-swollen starch granules can be considered not only as hydrogel particles, but also as potentially cost-effective dry-strength additives. Although the spray application of uncooked starch onto the wet web of paper, just before the wet-pressing and drying stages, has been practiced for many years, it still represents a game-changing option when there is an urgent need to greatly increase the bonding strength of paper (Proctor and Reid 1974; Davies 1977). The application technology can be quite simple – such as a spray-boom extended across the width of a Fourdrinier paper machine forming table. Alternatively, the starch granules can be applied in a falling curtain of water (Fougler and Parisian 1999). As another option, the uncooked starch can be added at the wet end of the paper machine, using retention aids to retain the particles (Greenwood 1999). In any such system, Wielema and Brouwer (2003) reasoned that the drying process of a conventional paper machine does not offer a sufficiently intense combination of temperature, time, and moisture content to allow more than a partial swelling and cooking of the starch granules before the completion of drying. But on the positive side, uncooked starch is relatively inexpensive, and the amount added to the system does not have to depend on the adsorption capacity of the fiber surfaces.

Further promising results with hydrogels as dry-strength agents were obtained by Pelton and co-authors (Miao *et al.* 2007, 2008; Wen and Pelton 2012). Miao *et al.* (2007) found that 1.5 µm hydrogel particles gave substantially higher wet tensile strength as well as dry strength of softwood kraft sheets compared to a similar mass of linear polyelectrolyte of the same type added to the fiber suspension. The difference was attributed to the ability to retain a thicker layer of polymer at the fiber surfaces, and also to the fact that the hydrogels were much too large to permeate into the cell walls of fibers. When comparing different sizes of hydrogel and different degrees of cross-linking, the most promising results were with the smallest hydrogels and the lowest levels of crosslinking (Miao *et al.* 2008). In follow-up work involving the adhesion of cellulose films, Wen and Pelton (2012) showed that acrylamide-based hydrogel particles in the diameter range of 0.3 to 4.5 µm were advantageous for achieving strengthening effects at low polymer dosage, consistent with more efficient coverage of surfaces. But larger hydrogel particles were advantageous for achieving high increases in dry strength at relatively high addition levels, consistent with an ability to get more polymer into the bonding areas. Notably, the results did not depend on the size of the cationic vinylamine polyelectrolytes that were used to coat the negatively charged hydrogels and make them adhere to the fibers – only the size of the gel particles themselves. However, practical concerns such as stickiness and costs can be expected to place constraints on both the size and amount of hydrogel material that is used in wet-end applications (Heermann *et al.* 2006). Another concern is that hydrogels, by definition, contain a lot of water. It follows that an increased need to evaporate water might slow the production rate or raise the cost of production when using a hydrogel-based strategy for increasing paper's dry strength.

Bonding Strategies for High Humidity Applications

Due to the hydrophilic nature of cellulosic fibers, and in particular the high dependency of paper structures on hydrogen bonding as a major contribution to dry strength, conditions of high humidity and contact with aqueous liquids represent particular challenges for papermakers. The subsections that follow consider publications dealing with a wide range of strategies that papermakers have employed to maintain paper strength as the moisture content of the paper increases. The hydrophobic sizing of paper, which has been reviewed elsewhere (Hubbe 2007a; Lindström and Larsson 2008), will not be considered here. In an effort to achieve humidity-resistant bonding between cellulosic fibers, it makes sense to try to supplement or replace hydrogen bonding as the main contribution to bonding within paper.

Wet-strength treatments and paper performance at high humidity

High humidity is not the same thing as soaking. Yet it is logical to assume that a treatment providing strength to paper when it is thoroughly wet might also bolster its strength under humid conditions. The idea is to supplement hydrogen bonding in paper with moisture-resistant kinds of bonding. Some such treatments fall into the category of "wet strength" strategies, about much has been written (Espy 1995; Lindström *et al.* 2005; Obokata and Isogai 2009; Ozaki 2011; Su *et al.* 2012). Strong wet-strength gains in addition to dry-strength gains have been reported in cases where conventional wet-strength agents were added to suspensions of fibers that had been treated in some way to increase their carboxylic acid content (Ahola *et al.* 2008). It is generally agreed that wet-strength treatments involve three-dimensional crosslinking of the resin with itself, a process that can be expected to envelope and hold onto fine cellulosic fibrils and polymer chains extending into the resin from the two adjacent fiber surfaces (Espy 1995; Hagiopol and Johnston 2012). Such a mechanism is illustrated in Fig. 13. The cationic nature of typical poly-amidoamine-epichlorohydrin wet-strength resins can be expected to encourage such three-dimensional incorporation of cellulosic polymer segments in the resin during paper formation and drying. As shown in the figure, one can envision a cross-linked mass of polymer chains that incorporate fibrils extending from the adjacent fiber surfaces. It is also likely that the amidoamine-epichlorohydrin resins covalently bond to carboxyl groups on the fiber surfaces as part of the curing mechanism (Espy 1995; Hagiopol and Johnston 2012).

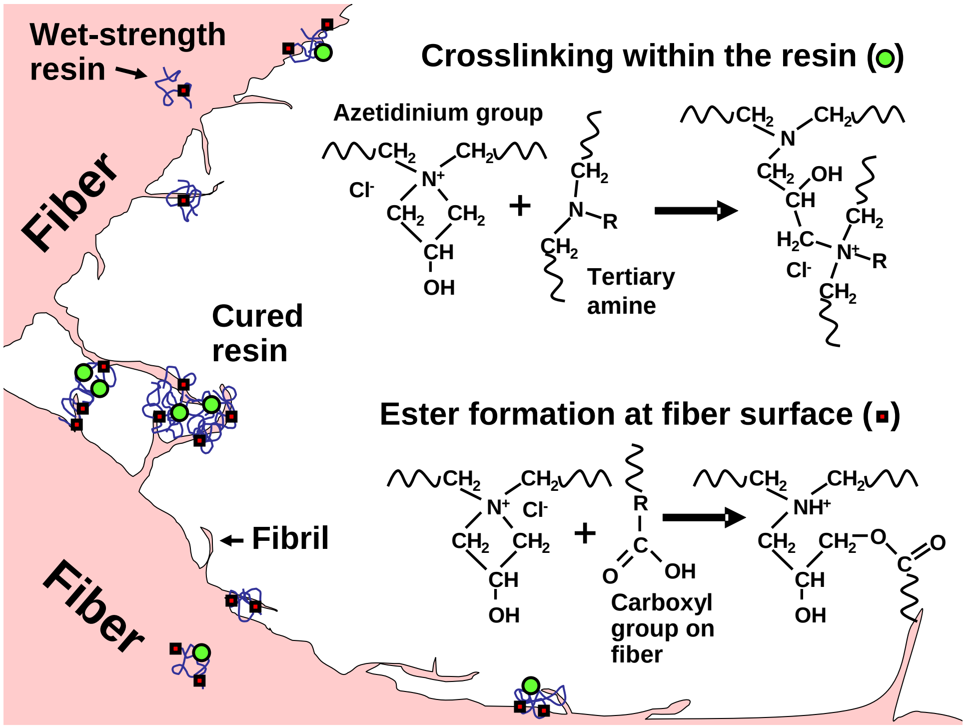

Fig. 13. Three-dimensional covalent crosslinking during the "curing" of a conventional wet-strength resin, resulting in a hardened mass that incorporates cellulosic chains and nanofibrils from the adjacent two fibers. Filled (green) circles represent crosslink point. Squares (red) represent ester links between the resin and carboxylic groups associated with the fiber.

Boonyasarn *et al.* (1992) showed that although wet-strength treatment of paperboard, in combination with some other measures, can significantly increase the dry strength of paper, essentially all of the dry-strength gains are lost relative to ordinary paperboard when the testing is carried out under high humidity conditions. In other words, although wet-strength agents can keep the strength of paper from falling to zero in the soaked condition, they fail to protect the pervasively hydrogen-bonded structure of paper from the effects of high humidity. Other measures employed by the cited authors, in an attempt to produce humidity-resistant premium paperboard, were increased refining, increased cross-machine fiber orientation, an increased proportion of virgin kraft fibers, and extended-nip pressing. While all of these listed measures can be expected to contribute to the manufacture of a premium-quality paperboard product, none of them deals effectively with problems related to the decreasing modulus of elasticity of cellulosic materials as the humidity and moisture content are increased.

Cross-linking has been considered in some recent studies involving innovative dry-strength treatments. Horvath *et al.* (2010) observed improved performance of cationic dextran as a dry-strength additive under low humidity conditions when it contained acetal groups capable of crosslinking. Surprisingly, however, the crosslinking yielded no benefit when the paper was tested at high humidity; the authors suggested that a stiff "joint" between two bonded fibers cannot be effective if the surrounding material has been softened by moisture. This is a shame, since the hemiacetal bonds formed by aldehyde groups during the drying of paper are reversible after thorough rewetting, allowing excellent recyclability and restoration of temporary wet-strength properties in the recycled paper (Farley 1994; Chen *et al.* 2002; Hagiopol and Johnston 2012). The formation of covalent amide linkages is possibly significant during the thermal curing of paper that has been treated with polyelectrolytes bearing both amine groups and carboxyl groups (Eriksson *et al.* 2006). Whether or not such covalent bonding reaches significant levels during ordinary papermaking has not been established, and again there is no assurance that such bonds would positively affect paper's performance at high humidity.

Polyelectrolyte complexes and tolerance to high humidity

Papermakers have observed for many years that treatment of the fiber furnish with certain highly-charged cationic polyelectrolytes can lead to measurable increases in residual strength after the paper has been fully wetted (Trout 1951; Espy 1995). Aarne *et al.* (2012a) observed especially strong bonding when highly charged linear polyelectrolytes with amine groups in the main chain were added to suspensions of fibers that had been treated with the highly anionic polymer CMC. Marais and Wågberg (2012) observed similar effects when polyallylamine or polyvinylamine were added to unbleached kraft stock, followed by heat-curing of the paper. Gärdlund *et al.* (2005) observed that wet-strength effects could be achieved by addition of polyelectrolyte complexes (PECs), but only if the paper was subjected to heat treatment. One possible explanation of the beneficial effect of thermal treatment is that components such as lignin are temporarily softened, and that those components, possibly with interaction with other additives, engage in a curing effect when the temperature falls below their glass transition point (Salmén 1986). Linhart (2005) suggested that the wet-strengthening effects induced by highly cationic polymers in mixtures of negatively charged fibers are due to a de-swelling effect. This is basically the same mechanism by which polyelectrolyte complexes generally show a minimum of swelling in the charge-balanced condition (Michaels 1965). At the charge-neutral condition of a PEC, there is a minimization of osmotic effects that might swell the fibers. In view of the progress that has been achieved in the studies just cited, *in-situ* complexation between oppositely charged polyelectrolytes deserves increased study relative to increasing the humidity-tolerance of paper products.

Aarne *et al.* (2013) recently explored the use of amphiphilic diblock copolymers as a way to hydrophobize paper. A strong hydrophobic sizing effect was found with triblock copolymers having relatively short cationic end-chains and a relatively long hydrophobic central block. The cationic functionality ensured efficient retention of the additive during papermaking. The large central block was found to provide strong hydrophobization when the paper was dried with sufficient heat to melt the additive. It is not yet known whether such additives might improve the humidity-tolerance of paper products.

Impregnation with silicate

Another approach that has been used to strengthen paperboard products and to improve their performance under humid conditions has involved impregnation with a solution of sodium silicate (Walthy 1987). The cited author describes equipment that can be used, as well as presenting some test results. Impregnation with sufficiently high levels of sodium silicate made it possible, for instance, to achieve the compression strength expected for a 69-lb (337 g/m^2) linerboard at a much lower basis weight of 42-lb per ream (196 g/m^2). The author suggested that the solubility of sodium silicate is a major concern, presumably making such systems vulnerable to failure upon wetting. Given the promising results shown in the cited work, and also noting the widespread success of cellulose-reinforced cement products (Jorge *et al.* 2004; Brandt 2008; Karade 2010), it is recommended that more research be carried out related to the development of mineral-reinforced paperboard. It appears that there is a critical need for industrial and academic research to make further progress in this important branch of technology.

Cellulose nanocrystal coalescence as a dry-strength strategy

Co-crystallization at the interface between cellulosic surfaces (Nazhad and Pazner 1994; Wang *et al.* 2003; Newman 2004; Pönni *et al.* 2012) might be viewed as a possible strategy to achieve moisture-resistant bonding. The concept can be regarded as a proposed mechanism, for which the evidence has not been well developed. The approach can take its inspiration from the insolubility and dimensional stability of natural wood, in which the majority of the cellulose component is expected to be associated with crystalline nano-domains. Lindström (1986b) proposed that fibrillar aggregation and the coalescence of adjacent nanocrystals could account for contraction of the honeycomb nanostructure of kraft fibers upon drying, thus decreasing their ability to swell. This is basically the same mechanism as was proposed by Laine *et al.* (2006) to explain the essentially irreversible attachment of CMC to fibers under suitable conditions of high temperature, salt concentration, and time. Yuan *et al.* (2013) presented intriguing evidence that the state of crystallinity may also be affected by the refining of pulp, followed by drying under TAPPI standard conditions. All of these findings prompt the question as to whether it is feasible to put the same mechanism to work in creating durable bonds *between* fibers, rather than just within them.

In theory, a strong and moisture-resistant contribution to bonding would result if cellulosic crystallites were able to grow at the interface between two fibers in paper, resulting in coalescence of cellulosic chain segments. However, it is not certain whether or not the conditions present during the drying of paper are suitable for the type and extent of microfibrillar coalescence that would contribute to inter-fiber bonding. The predominant temperature of paper during the drying of paper, especially while the web still contains a substantial amount of water, is bounded by the boiling point of water. By contrast, Hattula (1986) observed that temperatures in the range 100 to 150 ^{o}C were needed in order to significantly increase the degree of crystallinity of cellulose within thermomechanical pulp or dissolving pulp fibers. On the other hand, NMR-based studies by Newman and Hemmingson (1997) and Newman (2004) detected co-crystallization, *i.e.* the coalescence of adjacent crystallites, during the first drying cycle of freshly pulped kraft fibers. Sheikhi *et al.* (2010) found similar results in the case of sugarcane bagasse fibers. It is important to note that the cited findings can be explained by closing up of pores *within* rather than *between* cellulosic fibers. Because of the manner of biosynthesis of cellulose within fibers, many of the cellulose chains within the cell wall of a kraft-pulped fiber already can be expected to be approximately in the ideal state of alignment with each other so as to allow healing between adjacent cellulose crystallites. In any case, conventional drying of paper can be expected to yield paper having ordinary properties, including substantially reversible hydrogen bonding between the fibers, allowing non-wet-strengthened paper to be readily repulped after placement into water.

Elements of a possible strategy to induce cellulose nanofibrillar coalescence at fiber junctions during the formation of paper can be drawn from published work. The term “zipper” can be used to describe the manner in which hydrogen bonding could be expected to take place between adjacent cellulosic surfaces, starting at one end and then progressing forward to achieve neatly repeating registration and efficient hydrogen bonding between adjacent cellulose chains (Hubbe 2010). For example, Akagane *et al.* (1979) proposed a concept of multicenter hydrogen bonding to account for the bonding contribution of a DNA-inspired imidazolic polymer that was sprayed onto handsheets as a solution. Although the relatively low energy associated with each individual hydrogen bond is not sufficient to create a permanent attachment, the multiple and regularly repeating hydrogen bonds in a cellulosic structure can be very hard to disrupt. In order for this to happen at the interfaces between fibers during the drying of paper, the cellulose needs to be in a suitable form. One approach may involve the use of low-mass cellulose chains in some fashion. Kato and Cameron (1999) noted that the hydrolytic breaking down of long cellulose chains might promote more rapid crystallization. The idea is that short polymeric chains can more easily change their molecular conformation, including their lying down flat to be incorporated into a crystalline arrangement.

Based on such findings, there appears to be a need for research in which a suitably derivatized form of cellulose becomes regenerated *in-situ* only when the paper web is strongly heated in the course of drying. The first step would be to prepare a meta-stable, water-soluble derivative of cellulose that reverts to cellulose form under the conditions of drying of paper. In other words, the substituent group should be susceptible to rapid hydrolysis under hot conditions. Presumably such nacent cellulose chains would tend to quickly engage in crystal-forming interactions with all nearby surfaces. An illustration of such a mechanism is given in Fig. 14, which is based on the hydrogen bonding arrangement shown by Dinwoodie (1975). If such crystallization is able to bridge between adjacent fiber surfaces, then one could expect a welding together of adjacent fibers. Effects on wet-strength development, as well as questions about recyclability, would need to be resolved.

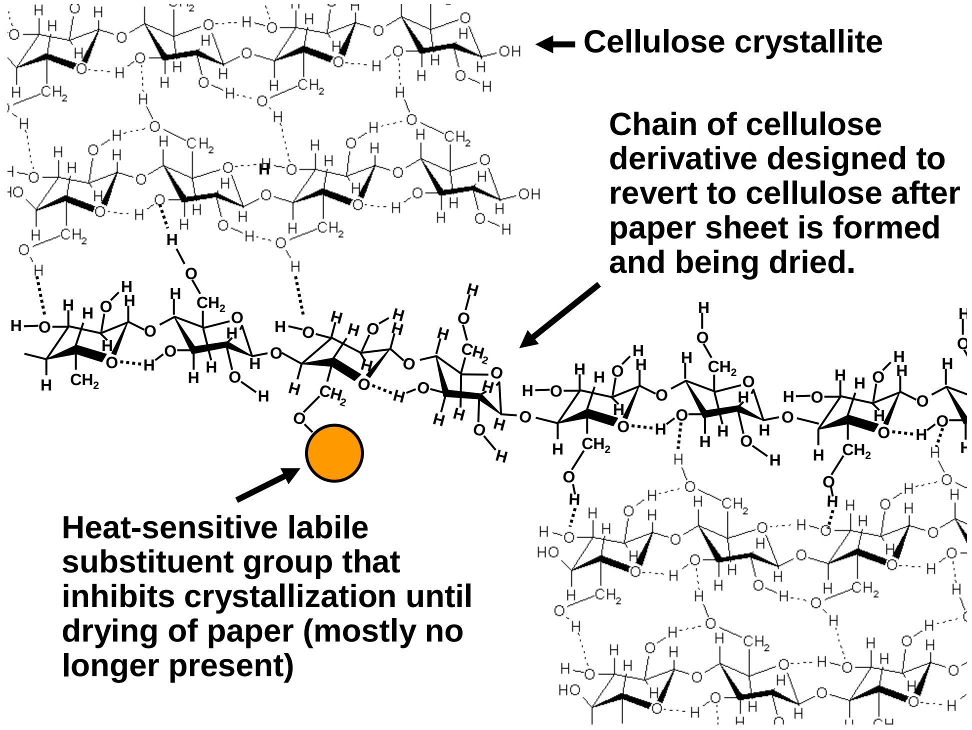

Fig. 14. Suggested mechanism whereby a suitably designed water-soluble derivative of cellulose becomes regenerated back to its crystallizable cellulose form *in situ* after the paper sheet has been formed only when subjected to the intense heating associated with the drying of paper

Covalent bonding to prevent unraveling of an extensively hydrogen-bonded system

It is possible that covalent bonds, such as ester bonds within a cellulosic material might act to prevent unraveling of a hydrogen-bonded structure, acting something like the "stop" at the end of a zipper. As noted by Ruffini (1966) and Laine *et al.* (2000), if sufficient heat is applied to paper that has been treated with CMC, then very high paper strength can be achieved. The effect is consistent with ester formation between the carboxylic acid groups and –OH groups at the fiber surfaces. The conditions required for significant ester formation tend to be somewhat more intense than what paper experiences during conventional drying procedures.

As mentioned earlier, one type of bond that is much more likely to become fully cured during the drying of paper is the hemi-acetal bond – a type of bonding that is employed in so-called temporary wet-strength agents (Chen *et al.* 2002). The cited authors found that wet-strength development was favored by low pH, as might be expected for the formation of hemi-acetal bonds. Aracri *et al* (2012) suggested that such bonds might account for observed wet-strength effects when paper was prepared after TEMPO-mediated oxidation of the fibers. Depending on the conditions of oxidation, such procedures may lead to different proportions of aldehyde and carboxyl functions on the treated material (Isogai and Kato 1998; Isogai *et al.* 2010). Laleg and Pikulik (1993a,b) described use of cationic starches having sufficient aldehyde group content to provide wet strength. Xu *et al.* (2006) described the treatment of papermaking furnish with polycarboxylic acids and glutaraldehyde/poly(vinyl alcohol) to create cross-linking and wet strength development. There has been a need for research to demonstrate whether or not such covalent bonds might be able to block the unraveling of an adjacent sequence, planar assemblage, or three-dimensional structure in which multiple hydrogen bonds keep two fibers from peeling apart.

A more aggressive approach can be based on the use of so-called "permanent" wet-strength agents such as poly-(amidoamine-epichlorohydrin) resins. Thus, Kitaoka *et al.* (1999) and Laine *et al.* (2003b) observed very strong bonding when such a resin was added to fibers that had been carboxylated by TEMPO-mediated oxidation. Su *et al.* (2012) were among many researchers who have observed development of increased dry strength in addition to wet strength when permanent wet-strength agents are used. However, as already noted at the start of this section, conventional wet-strength treatments have not been noted as being promising for paper's dry strength in highly humid situations.

"Enzymatic" bonds

A particularly creative way to achieve dry-strength improvements among fibers in paper involves the use of cellulase binding domains (Kitaoka and Tanaka 2001; Pala *et al.* 2001). The bonding agent employed in the cited studies consisted of a non-catalytic fragment of a cellulase protein complex. Though enzymes, like other molecules, ultimately must interact by means of electrostatic forces, van der Waals forces, and hydrogen bonding, *etc.*, what makes them somewhat unique is their specific molecular topography that can bind with a "lock-and-key" precision to certain substrates, with high specificity. Yokota *et al.* (2009) reported related work in which cellulose binding domains fixed onto an acrylamide-type polymer chain were able to act as an effective dry-strength aid, achieving high retention efficiency on the fibers. Pala *et al.* (2001), in their study employing deactivated enzymes, observed not only increased dry strength, but also faster dewatering. Since none of these system involved active enzymes, the effects have to be attributed to the proteins at the fiber surfaces acting as bonding agents. Whether or not such approaches can improve paper's performance under high-humidity conditions has not been established.

Chemical reaction after formation of a paper sheet

Chemical treatment of an already-formed sheet of paper has not often been considered in the literature. This is possibly due to inconvenient aspects of such procedures. As an exception, such a treatment scheme for a web of paper has been widely used for many years in the preparation of vulcanized or parchmentized paper (Van Ommen 1969; van der Reyden *et al.* 1993; Cartier *et al.* 1994; Toyo 2013). Such processing involves passing several layers of the paper together through a bath of concentrated acid (gelatinization), followed by extensive rinsing, then drying on steam-heated cylinders. The resulting sheets have been shown to have substantial resistance to delamination between the plies, in addition to high bonding strength and water resistance. Substantial wet strength is observed, even though no wet strength agent is used. These attributes appear to be consistent with the earlier discussion of microfibrillar coalescence. In other words, it appears that the treatment somehow activates the cellulose such that it is then able to join adjacent fiber surfaces together more effectively upon redrying. Notably, Cartier *et al.* (1994) found evidence that the fibers within parchmentized sheets are held together by poorly crystallized cellulose II. Some key barriers to implementation of this type of technology include relatively slow production speeds and brittle and translucent nature of the product, relative to typical uses of paper. Soltani *et al.* (2013) showed that some related properties can be achieved through the acetylation of paper after it has been formed. Water absorption was strongly suppressed, whereas fold and burst resistances were increased.

INCREASING DRY STRENGTH BY CHANGING HOW PAPER IS MADE

This section of the article will consider the unit operations of papermaking. Emphasis will be placed on how such operations might be reconfigured in ways that may achieve substantial improvements in paper strength. Presumably if the paper strength properties can be increased, then less virgin fiber would be needed to meet the requirements for different grades of paper. In general, an efficient system with a minimization of additive levels will provide a basis for low production costs. The task of finding the most efficient solution may be complex, as it requires that the conditions through the whole paper process are chosen in coordination with the different fiber alternatives and additives. Minimization of variations in paper properties needs to be a key focus, since it is often the lowest strength values, rather than the averages, that determine the amounts and qualities of fibers that are needed to meet strength specifications. For those readers who want additional background, the following sources give basic information about processing equipment and its usage for the manufacture of pulp and paper (Thorp 1991; Smook 1992; Biermann 1996; Gavalin 1998).

Advances in Refining of Cellulosic Fibers

Once choices have been made regarding the types of cellulosic fibers and the pulping procedures, the next critical issue affecting paper strength involves how the fibers are mechanically treated before papermaking, *i.e.* the refining process. Background information about modern refining methods have been reviewed (Baker 1995, 2000; Paulapuro 2000). To a large extent the effects of refining can be understood based on the concepts of fiber conformability, as it affects relative bonded area (Page 1969a). When applying these concepts, Batchelor *et al.* (1999) found that certain assumptions were needed in order to achieve good agreement when using Page's equation to predict paper strength. In particular, it was necessary to assume that fiber coarseness was not changed during conventional refining, even though some measurements may suggest otherwise.

There appears to be a consensus among paper technologists that dry-strength properties can be maximized by selecting an advantageous level of intensity of refining (Baker 2000). In other words, the ratio of applied force to the length of crossings of bars in a refiner should be appropriate for the type of fibers to be refined. Relatively high intensity, achieved my means of using a coarse plate pattern with fewer bars, can be expected to give suitable results for virgin softwood kraft fibers, which have relatively thick cell walls. By contrast, a lower intensity, achieved with a relatively fine plate pattern, would be needed for thin-walled fibers or for recycled kraft fibers. Excessively high intensity leads to substantial "fiber cutting," *i.e.* the reduction of fiber length. Too low intensity (which may be achieved in the case of softwood fibers) may fail to develop the fibers, probably because they experience only elastic strain (Croney *et al.* 1999).

Strategies for the refining of recycled fibers have been considered by various authors (Baker 2000; Zhang *et al.* 2004a; Wan *et al.* 2011; Olejnik *et al.* 2012). Oljenik found that removal of fines, followed by refining of the long-fiber portion yielded the most promising results. Notably, these results parallel those obtained much earlier by

Brecht (1947), who warned not to over-refine recycled kraft fibers. As noted by McKee (1971), higher levels of refining may imply less potential for strength gains to be achieved in subsequent cycles by further refining of the fibers Osovskaya and Poltoratskii (1999) found surprisingly that freezing of fiber suspensions can yield a refining effect, leading to increased strength properties for the once-frozen pulp fibers. Such results suggest a process in which the growth of ice crystals can provide an alternative means of bringing about delamination within the cell walls of fibers, thus providing a gentle refining effect. Higher consistency refining has been shown to deliver better outcomes in certain cases (Manfredi and Claudio-Da-Silva 1986; Lundin *et al.* 2008). Also it should be noted that bar sharpness, which can be affected by wear and pulp cleanliness, can affect the outcome, with sharper bars generally yielding stronger refined pulp (Berger 1997).

Two particularly interesting options for future development have arisen out of a focus on the surface-specificity of refining. On the one hand, it is possible to employ low-intensity treatment that relies mainly on repeated compression of fibers; such processing can be expected to internally delaminate papermaking fibers with a minimization of external fibrillation of the fiber surfaces (Wild 1998; Seo *et al.* 2000; Ghosh and Vanderhoek 2001; Wang *et al.* 2003; Le Ny and Messmer 2007). For instance, Seo *et al.* (2000) showed that "impact refining," carried out by striking a slurry of fibers repeatedly with a rod, was able to promote bonding without loss of fiber length; the described method appears to be essentially the same as the traditional method most widely used around the world for the manual preparation of fibers for papermaking before the invention of modern refining technology (Hubbe and Bowden 2009). On the other hand, refining can be carried out by passing the fibers between a rotor and stator having abrasive surfaces; such treatment can be expected to promote fibrillation of the surfaces, and it is possible to minimize the internal delamination (Kang and Paulapuro 2006; Wang *et al.* 2007a; Somboon and Pynnonen 2008; Somboon *et al.* 2009a,b). The external fibrillation was found to increase not only tensile strength and delamination resistance of paper, but it also tended to increase paper density somewhat, consistent with tighter bonding. A potential advantage of imparting mainly external fibrillation is that one can minimize damage to the internal parts of the fiber. In that way, one can preserve the fiber's inherent strength not only for the paper product being made, but also for later generations of recycled paper products.

Cellulosic fines removal or addition

Given the limited ability of most recycled kraft fibers to accept further refining, it makes sense to reconsider an approach described over 65 years ago by Brecht (1947). It was found that highly fibrillated cellulosic fines, prepared by refining, can be used as an alternative bonding agent. Brecht and others have shown that the cellulosic fines present in recovered kraft furnish may contribute rather little to the inter-fiber bonding within the resulting paper (Brecht 1947; Laivins and Scallan 1995; Selder *et al.* 2002). By contrast, Brecht found that paper strength equal to that achieved during the first cycle of papermaking could be produced if one removed all of the recycled cellulosic fines and replaced them with freshly-prepared fibrillar fines. In principle, only a minor quantity of fresh cellulosic material would be needed in order to reach strength levels of commodity paper products, while avoiding over-refining and therefore preserving what is left of the inherent strength of the recycled fibers. Because results of such a strategy can be expected to depend strongly on the manner and extent of preparation of the fines, there is a critical need for related research.

It is likely that in the past papermakers have been discouraged from adding fines to papermaking furnish due to slower release of water from the wet web, which often translates into a slower rate of production. However, by use of modern chemical-based dewatering technologies (Hubbe 2005b; Hubbe and Heitmann 2007), as well as greater dewatering capabilities of modern paper forming equipment (Thorp 1991; Gavelin 1998; Lindström *et al.* 2009), such considerations may not be as much of a barrier as before. In addition, the recent advances in technologies related to nanocellulose, as mentioned earlier in this article (Peng *et al.* 2011; Ramires and Dufresne 2011; Chauhan and Chakrabarti 2012), can contribute either together with or as an alternative to the use of freshly-prepared cellulosic fines. Promising results, in term of dry strength, have been reported, especially when adding microfibrillated cellulose – a class of nanocellulose that retains high flexibility due to its content of amorphous cellulose (Ahola *et al.* 2008; Eriksen *et al.* 2008; Guimond *et al.* 2010; Joseleau *et al.* 2012; González *et al.* 2012).

Sheet forming and paper strength

The manner of forming of the paper web is known to have a large effect on paper's strength. Research related to the uniformity of formation of paper, concentrating on chemical factors, was considered in an earlier review article (Hubbe 2007b). But advances in this area also will depend on the associated equipment. State-of-the-art forming equipment for paper machines, as well as their effects on paper structure have been described (Swerin and Ödberg 1996; Norman 2000; Paulapuro 2000). Theoretical advances also have been achieved relative to the forming process (Aidun 1998a,b). Because machine-made paper is typically anisotropic, usually with a higher MD strength and modulus compared to the CD (Nordström and Norman 1995a,b; Nordström 2003c,e; Nordström 2006), it has been suggested to make general comparison of strength based on the geometric mean of MD and CD values (Htun and Fellers 1986).

Niskanen *et al.* (1998) noted that some of the most important advances in paper machine design from the standpoint of uniformity are gap formers and the use of flexible foils. The term "gap former" implies a forming section in which the jet of fiber suspension emerges from a hydraulic headbox and lands within the closing gap between a pair of forming fabrics (Thorp 1991; Gavelin 1998). Dewatering elements such as foils and forming blades adjacent to the forming fabrics in such systems have been shown to play a key role relative to the uniformity of the resulting paper (Swerin and Ödberg 1996). Lindström *et al.* (2009) developed a numerical model to simulate and explain the effects of dewatering elements on the paper structure as it passes through such a twin-wire system. The concentration gradient of the paper web was predicted to be relatively uniform across the thickness of the wet web, except at very low consistencies, throughout the dewatering process, which is consistent with a thickening mechanism of dewatering (Kershaw 1980; Niskanen *et al.* 1998). It should be noted, however, that a pure thickening mechanism is inconsistent with other observations, such as strongly uneven distributions of filler relative to the thickness dimension of paper (Zeilinger and Klein 1995).

Evidence from various studies suggests that it can be advantageous to form a paper sheet in a relatively gentle manner, teasing the water out gradually (Kershaw 1980; Manson 1991; Mitchell and Johnston 2003). In a typical Fourdrinier papermaking operation, water is removed by passing the forming fabric over a series of hydrofoils

(Manson 1991). Figure 15 provides a schematic view of a wet web of paper resting on a forming fabric as it passes over a hydrofoil of a Fourdrinier paper machine. The vertical deflection of the forming fabric is greatly exaggerated in the diagram in order to emphasize the effect of a vacuum effect between the trailing edge of the hydrofoil and the wet web of paper. During this passage the wet web is kept somewhat fluidized, and the web experiences thickening to some degree, rather than undergoing pure filtration (Kershaw 1980). In other words, the paper web increases in consistency throughout its whole thickness during the dewatering process. The action of the hydrofoils, depending on their design, spacing, and angular settings, can induce a localized repeated eruption and contraction of thickness within the wet paper. When well adjusted, such localized flow events can make the paper more uniform. According to Radvan *et al.* (1966), although filtration is the primary mechanism by which papermaking fibers arrange themselves during a typical papermaking operation, there can be some fluidization and rearrangement within the sheet as it is acted upon by dewatering elements such as foils. As a consequence, the resulting paper has a “mixed mode structure” in which some fibers are not lined up with the plane of the sheet. However, if the action of hydrofoils is too aggressive, causing droplets of water and fiber to be flung into the air for instance, then the integrity of the sheet is lost, and much lower strength results.

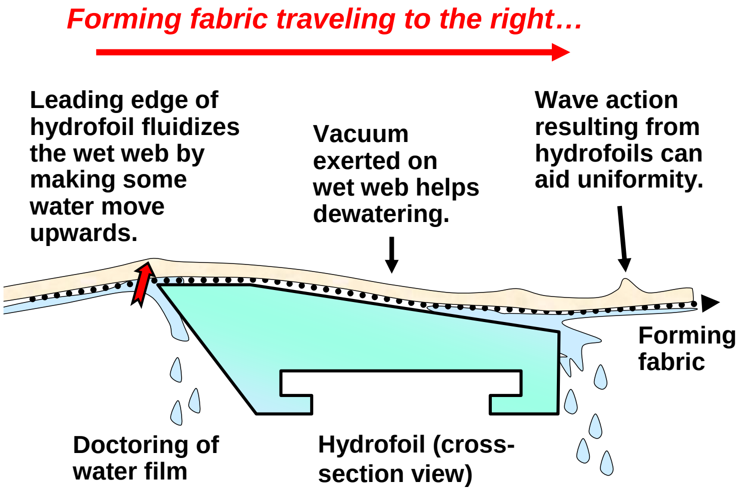

Fig. 15. Schematic illustration of hydrofoil action, promoting dewatering of a wet web during papermaking on a Fourdrinier machine. Fluidization and wave action, if not too severe, can promote paper uniformity.

Circumstantial evidence of the importance of nano-scale uniformity of formation can be drawn from studies in which paper strength properties were *not* well correlated with the results of formation tests, such as those based on image analysis. For instance Norman (1986) reported that sometimes a stronger sheet of paper is obtained when the aggressiveness of hydrofoil-induced action is reduced in intensity, even when the change results in a less uniform visual appearance of the paper. These results were confirmed and extended in later work (Nordström and Norman 1996; Nordström 2003a,b, 2006). In general, the highest strength performance has been associated with a twin-wire roll forming type of paper machine (Nordström and Norman 1995b); in such a design no forming blades are used so there is a minimum of disruption of the initially formed fiber mat. To account for such cases, it can be hypothesized that overly aggressive efforts to break up fiber flocs within a wet web of paper can have the unintended effect of disentangling associations between sub-microscopic fibrils on the adjacent fibers. Demonstration of such effects and the possibility of overcoming such effects can be expected to remain as great challenges for the coming generations of researchers and papermakers.

Advances in ply construction

Multi-ply paper forming equipment has been in use for many decades (Attwood 1991). For instance, there is widespread use of multi-ply “cylinder formers”, which are used in the production of relatively heavy-weight paperboard products. Likewise, Fourdrinier paper machines can be set up with secondary headboxes to produce a two-ply paperboard sheet. Alternatively, damp sheets produced simultaneously on two or three forming sections can be brought together and combined during wet-pressing. All of these options give papermakers potential opportunities to place brighter or stronger materials as the outside plies of the combined sheet to maximize, for instance, brightness and stiffness (Ranger 1967; Yang 1981; Haggblom-Ahnger 1998, 1999; Navaee-Ardeh and Nazhad 2008). In addition, inherently bulky fibers, such as chemithermomechanical pulp fibers, may be placed in inner plies to increase the caliper of the product; this can be a further means to enhance stiffness (Anon. 1976). In addition, if the material within or between plies has low resistance to tensile stress perpendicular to the plane of the sheet (so-called Z-directional strength), such construction can be optimized for retaining permanent folds, as in the case of folding boxboard grades. The mechanism of such folding was discussed in a review of handmade paper attributes (Hubbe and Bowden 2009). In some other paperboard grades it can be important that internal delamination be avoided. Different shrinkage of different plies within a multi-ply board can be the cause of undesired delamination or weakness.

Some more recent developments, which still have not received widespread implementation on a worldwide scale, involve ply construction in lower basis weight grades. Specialized headboxes are being used to deliver as many as three plies, most often with two different fiber compositions, into the same dewatering zone (Bristow and Pauler 1983; Gavelin 1998). As shown by Bristow and Pauler (1983), higher stiffness can be obtained by use of ply construction, despite the relatively low basis weights of the paper produced. Such results, along with other analysis of ply purity, indicate that the plies remain sufficiently well defined, even in the product, so that the desired effects can be achieved. Haggblom-Ahnger (1999) showed that xerographic copy paper can be made with higher stiffness, formation uniformity, and smoothness by placing the long fibers (needed for tensile strength) in a central ply and hardwood pulp in the outer plies. The same author (1998) found that other advantages could be achieved by selection of the filler and other additives for different plies. Such approaches, though well proven, have been implemented at a commercial scale only to a limited extent due to capital costs and the increased complexity of multi-ply operations.

Wet-pressing advances affecting paper strength

Without wet-pressing, most paper products would be unacceptably bulky and weak; however it is important to keep in mind that one of the prime motivations for the wet-pressing of paper is economic: If all the water remaining in the sheet after the forming section needed to be evaporated, then the production rate of most papermaking operations would be drastically lower, and the amount of energy needed to evaporate the water in the paper would far exceed the heat content of steam generated by incineration of pulping liquors, bark, and other materials in a typical pulp and paper operation. The equipment and procedures that can be used to press water out of the paper web have been reviewed (Reese 1991; Paulapuro 2000).

Effects of wet-pressing on paper strength are profound (Back 1987; Vainio and Paulapuro 2007a; Wan *et al.* 2011). As noted by Back (1987), pressing of dry paper, as in a calendering operation, usually has little beneficial effect on strength, if at all. By contrast, higher density achieved through wet-pressing has a high correlation with elastic modulus and related strength properties. Back (1987) recommended the application of steam to heat up the web of paper entering the press nip; such heating lowers the viscosity of the water, thus decreasing the resistance to flow from the paper into the press felts. To minimize densification, while still achieving favorable strength properties of paper grades requiring maintenance of relatively high caliper, Back (1987) recommended the use of double-felted nips or extended nips, which apply a somewhat lower nip pressure for a longer time period. All of the forementioned approaches allow more of the applied load in the press nip to be borne by the fibers, since less of the load is supported by hydraulic forces. In principle, the more effective pressing of the fibers, one against the next, can be expected to lead to greater bonded area.

Increased production rates when using extended nip presses have motivated developmental efforts, as well as some key publications (Pikulik 1999; Schlegel and Kaipila 2002; Lange and Meitner 2006; Hii *et al.* 2012). Danielsson (2002), among others, has reported that the structure of the press felt can have a major impact on the results achieved in an extended nip press. Hii *et al.* (2012) showed that there can be an advantage achieved by designing a press nip such that the sheet experiences increasing pressure almost to the point of exit. Such a profile of applied pressure was found to achieve not only higher solids of the emerging web, but also higher bulk in the resulting paper. By contrast, Pikulik (1999) observed lower strength following extended-nip pressing, compared with what could be achieved with conventional pressing. A less expensive, and therefore more widely implemented approach to extending the effective length of the nip has been through the use of relatively large press rolls (Kinnunen and Kiviranta 1992; Gavelin 1998). Lacasse (2012) described advances in the rubber covers used on such rolls to further increase the effective length of the nip.

Mathur *et al.* (1987) showed that to some extent it is possible to substitute more effective pressing in place of more refining to enhance paper strength. The combination can be economically attractive to papermakers, since both reduced refining and higher wet-pressing conditions tend to promote dewatering. Higher rates of production then can be achieved in dryer-limited paper machine systems.

Based on analysis of sheet structure following wet-pressing, it appears that there may be some potential to optimize the density profile within paper. Studies have shown that the surface of paper tends to become densified as it is pressed against an absorbent felt during its passage through a wet-press nip (MacGregor 1983a,b; Szikla and Paulapuro 1989). As illustrated in Fig. 16, the mechanism appears to involve the same balance of hydraulic and mechanical forces resisting compaction, as mentioned earlier. Flow of water out from the paper web and into the adjacent felt results in a localized decrease in the hydraulic pressure, such that the fibers are squashed more tightly against each other. In the center of the damp web, or adjacent to a non-felted roll surface, the hydraulic component remains high, so those parts of the sheet experience less compaction.

Probably due to challenging experimental aspects, not much research has been reported about effects of wet-end chemical conditions on the effects of wet-pressing. Torgnysdøtter and Wågberg (2004) observed that higher joint strength was achieved between fibers when pressing was carried out at higher salt concentration. The effects might be explained in terms of a less swollen condition of the fibers in the presence of salt, leading to a denser structure in the pressed zone. The authors noted that increasing salt concentration will tend to decrease electrostatic forces that would tend to resist compaction. Wegner (1987) attempted to find a relationship between treatment of furnish with a cationic acrylamide-based retention aid polymer and dewatering at a wet press. Though the polymer treatment was found to promote dewatering in the forming section of the paper machine, including a significant effect on vacuum dewatering, no significant effect on wet-pressing results was observed.

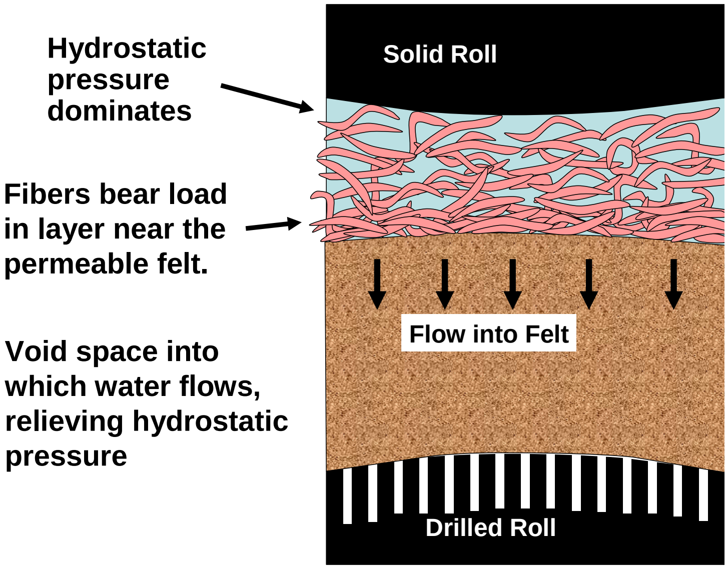

Fig. 16. Conceptual illustration of densification of paper's surface adjacent to a press felt during conventional wet-pressing in a single-felted press nip

Drying technology that can affect paper strength

If one walks along the length of a typical paper machine at a steady pace, the majority of time during that walk will have been spent adjacent to steam-heated cylinders devoted to the drying of paper. Another indication of the importance of the dryer section is the fact that paper's tensile strength increases by a factor of about 10 as it travels from the last of the wet-presses to the reel of the paper machine (Lyne and Gallay 1954). Figure 7, earlier in the article, illustrated an exponential increase of paper strength with increasing solids content in the range between about 44 and 93% (Kuhasalo *et al.* 2000). Background related to the drying of paper is available from various sources (Hill 1991; Smook 1992).

Regarding strength properties, one of the most important considerations during drying is the degree to which the paper is held in tension (Green 2006). One extreme is represented by "flash drying," a process in which fibers suspended in a current of air are allowed to shrink without constraint as they dry. Such fibers are good for producing bulky products such as fluff pulp for absorbent products, but the fibers are considered inferior for paper or paperboard products requiring high strength (de Ruvo and Htun

1983). Likewise, pulp sheets dried without restraint were found to yield lower-strength paper after they were reslurried (Mocchiutti *et al.* 2006). At the other extreme are typical paper machine systems in which the machine direction of paper is typically stretched by several percentage points in relative length (Barnet and Harvey 1980). The effects of drying tension also result in strong contrasts in the strength of laboratory sheets, depending on whether they are dried in a clamped position while adhering to a smooth surface, or if the sheets are allowed to shrink naturally (Higgins 2002; Green 2006). In each case, holding the paper in tension or slightly stretching it in the course of drying can be used as a strategy to increase the straightness of fiber segments in the resulting sheet (Page and Tydeman 1962; Vainio *et al.* 2007a,b; Retulainen *et al.* 1998). Htun (1986b) proposed that straining of the wet web also causes some machine-directional ordering of the fibers. By such means the tensile modulus and sheet stiffness can be increased, at least in the direction that was held in tension (Htun 1986b; Niskanen and Kärenlampi 1998; Retulainen *et al.* 1998). Meanwhile, properties requiring extensibility, such as resistance to impact and burst strength, can be decreased (Salminen *et al.* 1996). It is worth noting that the paper is completely restrained from stretching or shrinking in the plane for the sheet during the drying of many kinds of handmade papers (Hubbe and Bowden 2009) and when preparing test sheets to evaluate the strength potential of pulp at different refining levels (TAPPI Method 205). Such restraint is achieved by placing the damp sheet firmly against a smooth surface and not removing it until it is dry.

Restrained drying can be used as a strategy to improve paper’s dimensional stability in the presence of changing humidity conditions (Uesaka and Qi 1994; Vainio *et al.* 2007a,b). In an effort to further improve dimensional stability, Larsson and Wågberg (2008) carried out tests with a highly effective dry-strength chemical system. A polyelectrolyte multilayer (PEM) system was applied, as discussed earlier. In the case of sheets that were prevented from shrinking during the PEM bonding system made the sheets stronger but had no effect on dimensional stability. In the case of unconstrained drying, the resulting sheets were highly sensitive to humidity, even to a greater extent than the untreated sheets. Myllytie *et al.* (2009) found that different polymer treatments had different effects on the development of tension during drying.

Hot-pressing strategies and paper strength

An inherent problem associated with industrial drying on a paper machine is that there is relatively little restraint on the cross-directional contraction. At the same time the high temperatures associated with drying have been considered as a way to promote more effective removal of water from the sheet by application of pressure (Seth *et al.* 1985). These two ideas – applying heat and applying pressure – can be combined in a system called hot-pressing. Back (1987) showed that the combination can be expected to achieve higher sheet density, thus giving higher modulus. Related technologies can be called press-drying or impulse drying, depending on how the process is implemented.

Perhaps the best example of press drying involved laboratory conditions in which paperboard was dried between a smooth metal surface and blotter paper (Seth *et al.* 1985). For a wide range of cellulosic pulp types, higher tensile strength, modulus of elasticity, and edgewise compression strength were achieved under heated press-dried conditions in comparison to control tests in the same format but without heating applied during drying. The effects were partly attributed to a lower equilibrium moisture content of the press-dried paper. It was proposed that the lower moisture was due either to some kind of covalent crosslinking or to irreversible hydrogen bonding. In addition, in the case of fibers having relatively high content of lignin, the authors proposed that the results would be affected by flow of the hemicellulose-lignin matrix within the fibers. The latter proposal is consistent with the authors' observation of greater collapse of the lumen structure within the fibers of press-dried paper. The greatest advantage of press drying, according to the cited paper, is that higher sheet density can be achieved, thus reducing the amount of energy needed to refine the fibers to achieve bonding. Also it was proposed that some resistance to humid conditions might be provided either by the flow of the matrix materials during wet-pressing or by auto-crosslinking reactions. Such reactions might include ester formation (see Laine *et al.* 2000) or the coalescence of crystalline domains, as discussed earlier (see Pönni *et al.* 2012).

The term "impulse drying" has been applied to systems in which paper is passed through a nip in which one surface is hot and the other side of the sheet is against a porous felt. Such an arrangement provides volume for the escape and possible condensation of both water and steam from the paper web (Back 1991; Boerner and Orloff 1994; Larsson *et al.* 2001; Larsson and Orloff 2001; Lucisano *et al.* 2003). In principle, rapid evaporation of water at the heated surface can be expected to create superheated steam, which then tends to push water and steam through the sheet and out the other side. It appears that the main limiting factor discouraging implementation of the technology has been a tendency of the sheet to delaminate as it leaves the nip. Boerner and Orloff (1994) and Larsson and Stenstrom (1998) found that such delamination could be minimized by keeping the basis weight as well as the refining degree low. Unfortunately, those criteria rule out many products of greatest interest to papermakers. Larsson and Orloff (2001) found more promising results when using dwell times corresponding to extended nip pressing. Both paper dryness after the nip and the resulting paper strength were judged superior to what was achieved by conventional pressing, then drying. Mendes *et al.* (2002) found that though the use of cationic starch with impulse drying was able to enhance paper strength, it also worsened problems associated with sticking of the sheet to the hot surface.

Condebelt drying

In view of the interesting, but in the end problematic results that have been obtained with impulse drying, there has been sufficient motivation for researchers to consider using a radically different type of equipment. In particular, a key limitation of impulse drying, as described above, has been the relatively short time during which the web passes through a press nip. A longer exposure to heat and pressure would allow more opportunity for moisture to escape from the sheet without causing delamination. Such treatment has been effectively achieved at a commercial scale in the form of two production-scale installed drying systems having the trade name Condebelt (Kunnas *et al.* 1993; Retulainen 2003; Kiviranta *et al.* 2000). As diagrammed in Fig. 17, these systems work by drying the sheet in a sandwich between two solid steel belts, one heated and the other cooled. On the cooled side the sheet is backed by a course fabric, offering sufficient void volume within which condensate can collect.

Superior levels of elastic modulus have been routinely achieved by means of Condebelt drying, in particular when using relatively high-yield fibers. Kiviranta *et al.* (2000) estimated that the increases in compression strength can be sufficient to enable papermakers to reduce basis weights by about 20 to 30%. Such strength improvements can be important in such products as linerboard, which need to be able to support heavy loades in the stacking of corrugated boxes. Some of the effects that occur in the course of impulse drying or Condebelt drying appear to result from a combination of pressure and the thermal softening of lignin and hemicellulose in the presence of sufficient moisture (Back *et al.* 1967; Back and Salmén 1982; Irvine 1984). Kiviranta *et al.* (2000) estimated that the side of the sheet adjacent to the heated steel belt remains near to 120 °C for an extended period. By contrast, during conventional drying the paper web is expected to remain within the range of only about 65 to 75 °C for most of its passage through the dryers (Kiiskinen *et al.* 2000).

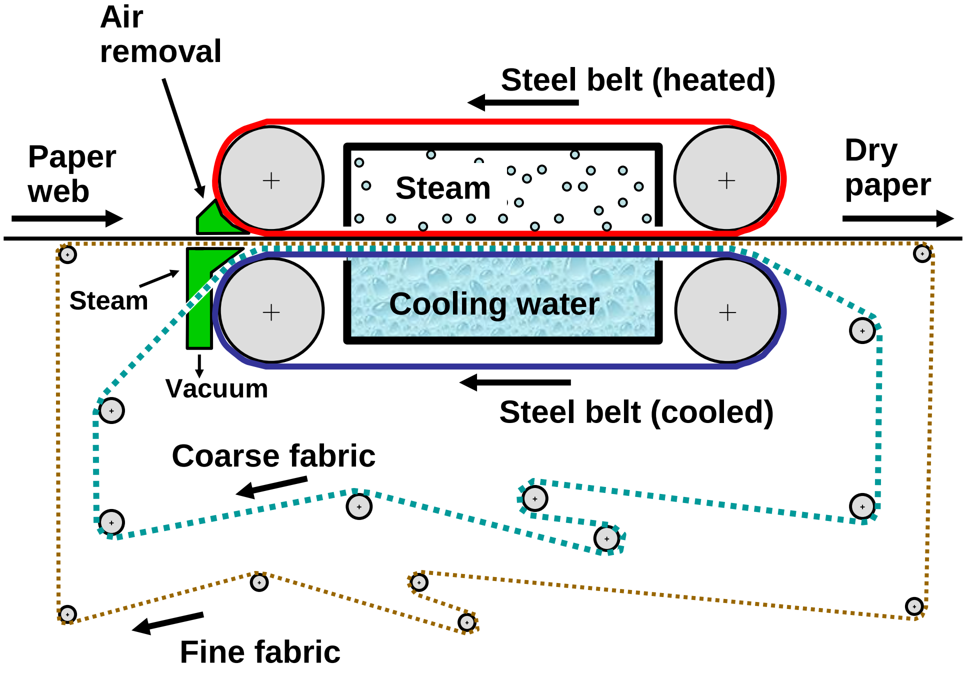

Fig. 17. Schematic drawing of Condebelt drying system (redrawn based on concept shown by Retulainen (2003)

Pynnönen *et al.* (2002) showed that even inherently very stiff high-temperature thermomechanical pulp (HTMP) fibers, which usually are quite deficient in bonding ability, are able to soften sufficiently in a Condebelt system so as to achieve good bonding. Microscopic analysis has revealed a tendency for greater deformation of individual fibers during Condebelt drying, with an intense densification at fiber crossing points (Kunnas *et al.* 1993).

Another factor that can be expected to contribute to the superior strength of Condebelt sheets is the fact that the web is prevented from shrinking at all in the plane of the sheet – either in the lengthwise or the crosswise direction – throughout the drying process (Kiviranta *et al* 2000). As a consequence, all of the fibers tend to become stretched, straightened, and to use a term from Giertz (1964), activated. In other words, an applied tensile stress will tend to be shared simultaneously by multiple fibers and bonded areas, rather than the stress being concentrated, thus causing early failure at points of stress concentration.

The intensive nature of the Condebelt system, as well has the high levels of bonding that are achieved, can lead to concern about the quality of the fibers after they are recycled (*e.g.* see Pycraft and Howarth 1980). Initial evaluations have not revealed greater loss of strength potential in comparison to the recycling of kraft paperboard that has been conventionally dried (Kiviranta *et al.* 2000). A likely explanation is that the tendency of the Condebelt drying system to hold the fibers straight and minimize kinks probably would compensate, to some degree, for the expected loss of bondability when kraft fibers are intensively dried (Weise 1998). Any overdrying effects may be mainly experienced by the upper layer of the sheet facing the heated steel belt; it is likely that the saturated steam temperature during Condebelt is mainly controlled by the temperature of the cooled belt and that over-drying is avoided for most of the sheet thickness. It has been shown that some reslushed Condebelt-dried paper can be stronger than cylinder-dried paper after recycling (Retulainen 2003). There was indication that the fibers were flattened by the Condebelt drying and that they remained flat after being dispersed in water. The consequence of such flattening can be a greater area of bonding between fibers in the recycled sheets. A potentially negative feature of Condebelt paper, depending on the proposed application, is that one side of the sheet will have a very pronounced pattern, *i.e.* very severe “wire mark”.

LIFE CYCLE ISSUES

As stated in the Introduction, the initial goal of this article has been to examine published information concerning how to achieve paper strength requirements with less use of freshly pulped cellulosic fibers, *i.e.* with lower basis weight, by using minerals in place of some of the fiber mass, or by using higher amounts of recycled fibers. As has been shown in the preceding pages, the literature gives evidence of a great deal of progress in achieving such goals. The present section deals with another kind of question – whether reducing the amount of virgin fiber used in papermaking is necessarily a net benefit to the environment. As will be shown, the evidence is mixed and there is a need for detailed life cycle assessments (LCAs) that take into account the unique features of different strength-enhancing strategies.

When attempting to judge environmental impacts, a primary question to address is whether or not cellulosic resources are likely to be utilized at a rate that exceeds their photosynthetic replacement. According to a report by the Pöyry company (2011), the proportion of fresh wood pulp in the fiber mix has been decreasing for many years, and by 2011 it had fallen to 41% of the materials used worldwide for papermaking. If one were to take into account the filler content of many paper grades, then the estimated proportion of fresh wood fibers would be yet lower. Furthermore, the absolute consumption of fresh wood pulp has been relatively unchanged since 1995. In Western Europe and North America the amount of wood harvested has decreased in recent years. As of 2010 the potential wood harvest is said to be greater than the actual wood harvest.

Even if one makes the assumption that the world will not soon reach its capacity to replace forest resources that are being used for pulp manufacture, there still are various other reasons that could justify efforts to reduce reliance on fresh fiber resources. These include possible reductions in fresh water consumption, reduced emissions to the air, reduced electrical energy consumption (partly by less need to refine the pulp), and reduced thermal energy consumption (partly due to higher dry solids content after wet pressing).

Hekkert *et al.* (2002) obtained LCA results showing that the production and consumption of paper products contribute to the emission of greenhouse gases. Various approaches to reducing such usage of resources were considered, including the use of thinner paper, more efficient printing methods, duplex copying, and printing on demand. The authors estimated that a 37% reduction in paper usage would have been theoretically possible over the course of the next dozen years by use of a combined approach. Lowering of basis weights was judged to be the most important opportunity. Print-on-demand technology was judged to be second in importance relative to its potential to conserve resources and avoid the production of greenhouse gases.

LCA studies invariably deal with choices. For instance, the recycling of paper to recover the fibers can be compared with other alternatives such as incineration or the substitution of reusable products in place of single-use products (Hubbe 2007c, 2008). Also there are various details to consider regarding how the processing of fibers during the initial pulping and papermaking may affect their ability to be recycled (Hubbe 2010). For example, as noted earlier, loss of hemicellulose during processing, especially when the paper is subjected to acidic conditions during papermaking, will tend to hurt the subsequent quality of the fibers after their recovery and repulping.

A combined optimization and simulation model by Bystrom and Lonnstedt (1997a) showed that a mix of production of paper from primary resources and from recycled paper made the best sense in the cases considered, though the results depended strongly on location. In southern Europe, where forest resources are limited, the model showed a minimization of environmental impact when 53% of the fiber is obtained by recycling. By contrast, in the Nordic countries the model predicted that a utilization rate of about 30% fibers from recycling would maximize environmental benefits. Another study by the same authors (Bystrom and Lonnstedt 1997b) showed that fiber recycling generally can be expected to have a negative impact on the environment due to its greater dependency on electrical energy from the grid. This is because, unlike the kraft pulping process, the operations cannot benefit from the fuel value obtained by the combustion of lignin and other organics in spent pulping liquor. The study results suggested that waste paper ought to be incinerated, with the production of electricity, thus displacing the use of fossil fuels used in power plants. Various other LCA studies have similarly concluded that incineration of used paper products, combined with recovery of their energy content, will yield a net environmental benefit compared to recycling (Gains and Stodolsky 1996). The cited authors made an exception in the case of used newspapers and corrugated containers, since in those cases the fibers are relatively easily recycled. Old newspaper (ONP) pulp can be readily made into recycled newsprint paper, and old corrugated container (OCC) pulp can be made into containerboard with relatively simple processing. As an alternative to incinerating the used paper, the cited authors also advocated the use of wastepaper resources for production of cellulosic insulation. Pajula and Kärnä (1995) predicted only marginal differences in sustainability outcomes based on LCA when comparing the use of virgin fibers, full recycling, and full use of incineration to recover the energy content of used paper. Remarkably, the incineration option was predicted to release lower net amounts of CO_2 and SO_2 than the recycling option. Both options were regarded as being far superior to landfilling, however, since landfilling was predicted to result in the release of substantial amounts of methane, nitrogen oxides, and chemical oxygen demand in typical installations.

Counsell and Allwood (2007) took a more imaginative approach to envisioning possible alternatives to current practices. Their analysis considered opportunities to bypass different stages in the conventional paper-based publishing cycle. Recycling of waste paper was compared relative to its incineration, landfilling, the use of freshly harvested fiber resources, and a hypothetical process that the authors called “un-printing". Of all of these options, un-printing was projected to have the highest potential benefit in terms of the environment. Unfortunately, it is not clear how one would actually implement a process of removing and then re-applying print to existing pieces of paper, which then would need to be reassembled into the proper format for distribution to the readers.

In view of the fact that many of the cited life-cycle studies cited above cast doubt on environmental benefits of paper recycling and related technologies, what then can be the justification for attempting to use less virgin fiber when making paper to meet various requirements? It turns out that there are several strong reasons:

- Life cycle assessment studies as cited above typically are based on an assumption that adequate supplies of harvestable wood or other plant material are presently available and that the current growth rates are sufficient to keep up with demand. The reality is that if all recycling operations were immediately converted to use of freshly pulped fibers, then there would be quite visible reductions in the amounts of standing timber in the world's forested areas. Though there have been some claims that the amount of harvestable timber has been stable in North America (AFPA 2013; Twosides 2013), throughout the world there has been a strong and persistent trend toward the loss of forested area and its conversion to agricultural land or for other human needs (Mather 2005; Humphreys 2006; Douglas and Simula 2010).
- The European Union has established a target to move to a sustainable, low-carbon bioeconomy by 2050 (CEPI 2011). Such efforts can be expected to result in scarcity and increased prices of virgin cellulosic materials.
- Though, in theory, yet higher levels of freshly pulped fiber can be sustainably produced from plantation forests and from other planted fiber sources, such as grasses, there are environmental costs to be considered in each such case. Plantation forestry typically requires substantial use of fertilizers and pesticides in order to meet the expectations of the growers (da Silva 2013; Menezes *et al.* 2012). Also there are concerns that the widespread planting of monoculture crops will fail to support the natural diversity of other plant and animal species that make up the world's natural environment (Bremer and Farley 2010; Hartmann *et al.* 2010).
- The chemical-based pulping facilities that would be needed to satisfy all of the world's present usage of cellulosic fiber based on fresh raw materials do not presently exist. A state-of-the-art pulping facility tends to be very large and can cost billions of dollars (Mitchell 1994; Anon. 2000; RISI 2012). Economy-of-scale issues are favoring the construction of very large pulping facilities, which then require raw materials to be transported longer distances (Gonzalez-Garcia *et al.* 2009). Though paper recycling facilities also entail high costs and often higher relative amounts of electricity (Merrild *et al.* 2009; Iosip *et al.* 2012), such facilities can be smaller (Koepenick 1995; Shearin 1995), a factor that can minimize transportation distances of collected materials.
- Finally, there can be wisdom in widely-held opinions. The public has learned, often as a result of personal experience that authoritative-sounding statements can later turn out to be unsupportable. Methods of life cycles assessment have not yet reached a level of reliability and uniform application that has been achieved in more mature fields of technology, such as engineering or chemistry. The jury of

public opinion still favors a frugal usage of the world's cellulosic fiber resources, and in the end we can expect the jury or public opinion to decide the case.

SUMMARY STATEMENTS

As illustrated in Fig. 18, publications considered in this review article have documented numerous promising steps that can be implemented either singly or in combination in order to reduce the amounts of freshly pulped cellulosic fibers that need to be used in the manufacture of particular paper products. As shown, various contributing measures can be implemented at many different stages of the process. Though the technologies to carry out many of these steps are already well known, others merit further research.

Because paper's strength depends on many different inter-dependent factors, one needs to be cautious when projecting benefits from a given improvement; strengthening a link in a chain may merely cause the chain to break elsewhere. The inherent physical properties of the fibers themselves, and fundamental aspects such as hydrogen bonding within cellulosic materials, imply that there will be "ceilings" beyond which it is not feasible to increase paper's strength. For instance, a recent study has shown that the maximum lengthwise strength of individual cellulosic crystals from wood is about 3 GPa (Saito *et al.* 2013). If a higher value is sought, then perhaps one needs to consider using something other than cellulose. Another danger is that exotic measures to enhance paper's strength may harm other attributes, such as ordinary paper's relatively low cost, its ability to be recycled, and its generally non-toxic nature.

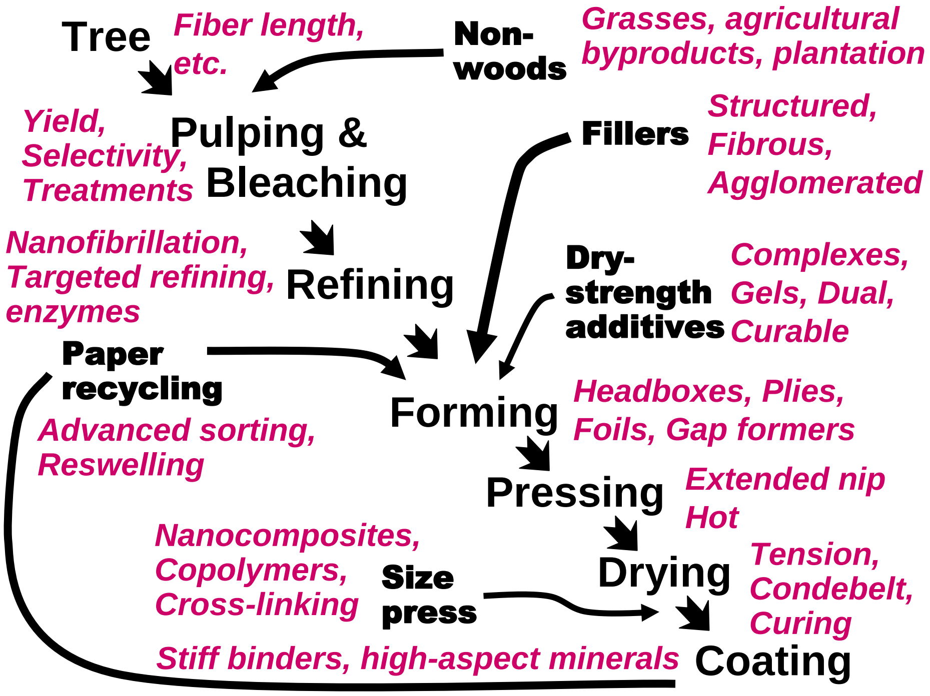

Fig. 18. Summary of promising contributions to increased fiber-efficiency of paper products and their broad distribution across the entire cycle of production

Numerical values given in Table A of the appendix can provide a general idea of the extent to which the main dry-strength properties (such as tensile breaking load) can be increased by various strategies that have been demonstrated in the literature. Commonly used measures such as refining are clearly very important. Also, it is clear that further strength gains by factors in the range between 1 and 2 can be achieved by use of a wide range of technologies. Some cautionary statements deserve to be repeated:

- The default conditions used in different studies cover a very wide range. In principle it is easier to achieve large gains in paper strength when using fibers that are initially deficient in inter-fiber bonding ability.
- Many of the individual strategies listed in Table A are either overlapping or mutually inconsistent. For instance, if inter-fiber bonding is improved by one means, then there may be limited additional benefits that can be achieved by simultaneously applying a different strategy to do the same thing.
- The nature of cellulosic materials imposes some inherent limits on the maximum strength of paper. Even if inter-fiber bonding is increased greatly, the strength of paper cannot exceed the combined strength of the component fibers.
- Certain strength-enhancing strategies may entail use of exotic chemistry that is not environmentally friendly.

A variety of potential profit-making opportunities are apparent from the present review, though each potential opportunity comes with its own set of costs and risks. To give just three examples, there are opportunities for chemical companies to produce the next generations of dry-strength agents. There are opportunities for other companies to improve such equipment as the fabrics used to transport paper during the drying of paper; higher and more uniform tension controls for such fabrics, as well as mechanisms to hold paper firmly against uni-run dryer fabrics, can be expected to decrease shrinkage of the paper, resulting in higher tensile modulus and other properties. And when dealing with discarded paper products, there are business opportunities related to the more efficient and effective sorting of mixed wastes, thus making it possible to direct each component of a mixed waste stream to its most valuable or its most environmentally justifiable usage (Iosip *et al.* 2010; Rahman *et al.* 2012; Ramasubramanian *et al.* 2012; Miranda *et al.* 2013).

Important advances in technology to reduce usage of fresh fibers in paper products are probably most likely to take place in grade segments that are relatively large and expanding. Examples include containerboard and carton board. The innovations most likely to see widespread adoption will be those that combine technological feasibility with high process efficiency and opportunities to save costs. Cost analysis could be considered as a focus of future studies and reviews.

One of the foremost challenges facing major initiatives to address the sustainability of papermaking operations may involve the communication of information in a form that evokes confidence and agreement – or at least acquiescence – from a public that has become somewhat jaded by conflicting statements about environmental issues. Because LCA studies are inherently complex and always include many simplifying assumptions, often not communicated to the general public, one can expect a natural distrust of findings that appear to support one scenario over another. In view of such public doubt, reductions in the amounts of virgin fiber that are used in meeting a given customer need for paper – especially fibers from natural forests – can serve as a practical proxy in place of deeper LCA work. Though reductions in the amounts of freshly-pulped fiber do not tell the full story, they at least are a concrete step from the viewpoint of a common citizen, who in the end will serve as the judge in a democratic system.

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Table A. Reported Relative Changes in Paper Strength Resulting from Various Treatments & Processes

Category	Base Condition	Modified Condition	Relative Change in Paper Strength	Reference
CMC	Bleached SW kraft fibers in Na form	Ionene treatment after CMC adsorption	2.0	Aarne *et al.* 2012
NFC	Bleached SW kraft fibers, sl. refined, Na	PAE resin, up to 10% content of nanofibers	2.2	Ahola *et al.* 2008
Fiber	Unbleached kraft pulp, unbeaten	Periodate oxidation of bleached kraft	1.13	Alince 1975
CStarch	Bleached SW kraft, refined, clay filler	Cationic starch for up to 50% filler content	2	Alince *et al.* 1990
Ionic	α-cellulose pulp with reactive dye	PEI spray onto dyed anionic fibers	1.6	Allan & Reif 1971
Pulping	Unbeaten softwood pulps, varied yields	Different yields, leading to higher density	1.6	Andreasson *et al.* 2003
Fiber	Sisal pulp with Na-AQ delignification	Laccase-TEMPO oxidation of the fibers	1.24	Aracri *et al.* 2012
Debond	Bleached HW kraft pulp, 575 mL CSF	Debonding agents, cat. surfactants	0.35 to 0.8	Asakura 2003
Pulping	Conventional kraft pulping conditions	Ultra-gentle pulping conditions	1.25	Atalla 1977
Press	Unbleached SW kraft, yields 50-70%	Increased intensity of pressing	2	Back 1987
Hemi	Bleached aspen kraft pulp, 45 ^{o}SR	Good effect already at 0.5% addition	1.16	Bai, Hu, & Xu 2012
Refining	HW & SW kraft pulps	Best results at low specific edge load	2.8 to 3.3	Baker 1995
Pulp	Unbeaten, never-drived bl. SW kraft	Carboxymethylation of fiber surfaces	2.5	Barzyk *et al.* 1997
CMC	Bl. SW kraft (outer layers)	Carboxymethylcellulose, 0.5%	1.3	Beghello *et al.* 1997
Hemi	Jute kraft pulp, CEH bleached, 30 ^{o}SR	Wet-end addition of hemicellulose	1.54	Bhaduri *et al.* 1995
DSAs	OCC pulp	Amphoteric starch with retention agent	1.9	Bhardwaj *et al.* 1997
Alkaline	Secondary sheets dried 105 ^{o}C 6 h	Alkaline treatment & shearing of pulp	1.16	Bhat *et al.* 1991
Hemis	Bl. HW kraft, 34 ^{o}SR	Cat. galactomannan	1.9	Bigand *et al.* 2013
Fiber	Bl. eucalyptus kraft, restrained drying	Carboxymethylation of eucalyptus pulp	1.55	Blomstedt *et al.* 2007
PEM	Bl. SW kraft, unrefined	Cat. starch, anionic. starch, cat. starch	1.7	Brännvall *et al.* 2007
Refining	Northern unbleached kraft pulp	Standard beater curves, also with recycling	6	Brecht 1947
Plies	Compared at same total composition	Multi-layer paper, stronger fiber on outside	1.15	Bristow & Pauler 1983
Filler	Calcium carbonate in printing paper	Preflocculation of whiting with cat. starch	1.2	Brooks & Meagher 1982
Dual	Corrugating medium, OCC	Anionic wet-end starch with PAC fixative	1.36	Brouwer 1997
CPAM	Five contrasting types of refined pulp	Cationic PAM, very high mass	1.03 to 1.69	Carlsson *et al.* 1977
PEC	Unbleached kraft, 480 mL CSF, pH 5.5	Amide wet-strength resin & starch xanthate	1.36	Carr *et al.* 1977
PEC	Linerboard and newsprint furnish	Amide wet-strength resin & starch xanthate	1.35 to 1.40	Carr *et al.* 1974

DSR	Old corrugated container pulp	Cationic and anionic acrylamide resins	1.5	Chan 1976
WSR	Whatman filter paper (impregnation)	Dextran with pendent acetaldehyde groups	4.5 (wet strength)	Chen, Hu, Pelton 2002
Filler	Bl. SW kraft, 17 °SR, CPAM reten. aid	3% $CaCO_3$ whisker addition	1.5	Chen, Qian, An 2011
PEM	Bl. HW kraft, unrefined, washed	PEMs: DADMAC, PSS, PAMs	1.75	Chin *et al.* 2012
Fiber	Multifibril angle of trees in typical range	Tensile index, lowest *vs.* highest MFA	1.3	Courchene *et al.* 2006
Xylan	SW kraft fibers, moderate refining	Adding high-mass xylan to kraft cook	1.1	Danielsson & Lindst. 2005
Spray	Linerboard, fluting, envelopes, wrapping	4% uncooked starch, spray application	1.12 to 1.53	Davies 1977
Filler	Bleached mix HW SW kraft, 14% filler	Starch modification of fillers	1.4	Deng *et al.* 2010
Hemi's	Bleached eucalyptus kraft	Xyloglucans, galatomannans addition	1.3	Denis *et al.* 2003
CMC	Once-dried bleached kraft fibers	CMC treatment before drying & reslurrying	2	Duker *et al.* 2008
CMC	Bleached, never-dried kraft fibers	CMC treatment, 2% by mass on fibers	2	Duker & Lindström 2008
PEM	Kraft fibers, refining level varied	PEC of Polyamidoamine/CMC	1.5	Enarsson & Wågberg 2007
MFC	Spruce thermomechanical pulp (TMP)	Microfibrillated bl. kraft pulp, 4% addition	1.2	Eriksen *et al.* 2008
PEM	Bl. SW kraft fibers, Na form, unrefined	PAH / PAA multilayers (8 layers)	1.6 to 2.0	Eriksson *et al.* 2005a
PEM	Bl. SW kraft fibers, Na form, unrefined	Cat starch/Anionic starch/Cat starch	2 to 2.7	Eriksson *et al.* 2005b
PEM	Bleached SW kraft	PAH / PAA multilayers, 8 total layers, heated	1.4 to 2.8	Eriksson *et al.* 2006
DSA	100% recycled container pulp	Cat starch or polyvinylamine (burst)	1.15 to 1.2	Esser *et al.* 2005
Filler	Conventional rosette-type PCC	Clustered prismatic optimized PCC filler	1.17	Fairchild 1992
GPAM	50:50 HW:SW bl. kraft, refined	Polyacrylamide and glyoxylated PAM	1.35	Farley
DSA	Old corrugated container (weaker of 2)	0.6 meq/g cationic polyvinyl alcohol	1.18 to 1.45	Fatehi *et al.* 2010
PEC	Sulfite pulp with removal of fines	PEC of chitosan and CMC (1% each)	1.6	Fatehi *et al.* 2009a
Bilayer	Sulfite pulp with removal of fines	Bilayer of chitosan and CMC (1% each)	1.2	Fatehi *et al.* 2009a
PVAm	Bleached sulfite SW	Cationic-mod. polyvinyl alcohols	1.28	Fatehi *et al.* 2009b
DSA	Bl. SW sulfite pulp	Cationic polyvinylalcohol (CPVA)	1.3	Fatehi & Xiao 2008
PEC	40% clay filler content	Cationic starch and anionic acrylamide	3	Fineman & Lindström 1985
CStarch	Bleached eucalyptus kraft, refined	Cationic starch (twice as effective as native)	1.2	Formento *et al.* 1994
Spray	Fine paper furnish, bl. HW & SW blend	2 to 9% curtain of uncooked corn starch	1.15 to 1.38	Fougler & Parisian 1999
Xylan	Virgin unbleached SW kraft, Na, fibers	Poly(allylamine HCl) & xylan two-layer	1.3	Galván *et al.* 2012
Bacter.	SW kraft dry-lap, unrefined	Bacterial cellulose	1.5	Gao *et al.* 2011
PEC	Unbleached kraft, no fines, Na form	Pre-formed PECs of PAH and PAA	1.14-1.53	Gärdlund *et al.* 2005
PEC	Relative to PAE cationic polymer alone	PEC with PAE & CMC in presence of salt	2.4	Gärdlund *et al.* 2003
CStarch	Northern bl. SW kraft, 40-mesh fraction	0.5% cationic starch at 500 mL CSF	1.4	Gaspar 1982
CStarch	Uncoated printing paper	Cationic potato starch, 1.5% dosage	1.2 to 1.3	Glittenberg 1993

NFC	Bl. eucalyptus kraft pulp, unbeaten	9% nanofibrillated cellulose added	2	González *et al.* 2012
Corona	Deacetylated cellulose acetate	Ozone treatment, then alkali	2 to 4	Goring & Suranyi 1969
DSAs	Recycling of pulp, no further treatment	Cat. Starch, cat. PAM, cat. & native starch	1.07	Grau *et al.* 1996
Lumen	Unbleached black spruce, 47% yield	Lumen loading TiO_2 at 13% ash, unbeaten	2	Green *et al.* 1982
NFC	25% clay in paper; SW TMP fibers	12.5% nanofibrillated bl. HW kraft, TEMPO	1.5	Guimond *et al.* 2010
Plies	Office paper, 30% SW, 70% HW	Multi-ply headbox use, CD stiffness	1.1	Haggblom-Ahnger 1999
DSAs	Bagasse soda pulp (not extracted)	Chitosan and cationic starch	1.1	Hamzeh *et al.* 2013
Xylan	Bleached eucalyptus kraft pulp	1% xylan retained on the pulp fibers	1.1-1.2	Han *et al.* 2012
Drying	Conventional drying, CD tensile stiffness	Cross-directional restraint	1.2	Hansson *et al.* 1989
Hemis	Spruce TMP, extracted	Galactomannans & galactoglucomannans	1.05 to 1.2	Hannuksela & H 2004
PEC	50:50 bl. HW, SW kraft, 470 mL CSF	Cat. graft starch & unmodified starch	1.1	Heath *et al.* 1974
PEC	70:30 bl.HW:SW kraft, 400 CSF no fines	Net addition of 10% polyelectrolytes, PEC	1.6	Heermann *et al.* 2006
CStarch	Four different pulp types	2% cationic starch addition to virgin pulp	1.6	Hipple 1991
CMC	Bl. sulfite 600 mL CSF	DS 0.3 to 0.45 CMC beater addition	1.4	Horsey 1947
XL	Never-dried semibleached kraft pulp	Cationic acetal dextran, crosslinking	1.5	Horvath *et al.* 2010
CStarch	Bl. SW kraft pulp, fibers only, unrefined	Cationic (quaternary) starch	1.25	Howard & Jowsey 1989
PEC	Non-bonding glass fibers	PECs *in-situ*, poly-DADMAC & CMC	>100	Hubbe 2005a
Dual	Unbleached SW kraft, never dried	Fiber surface saturation: DADMAC & CMC	1.26	Hubbe *et al.* 2003
Ampho	Bl. HW kraft, 440 mL CSF, fines free	Acylamide-based random polyampholytes	1.6	Hubbe *et al.* 2007a
Fiber	Bl. SW kraft, mechanically fluffed	Maleic anhydride gas-phase treatment	1.2	Hubbe *et al.* 1999
Coating	Standard coating clay (sheet tensile)	Highly platy coating clay	1.3	Husband *et al.* 2009
Saturat.	Kraft, NSSC, recycled fibers	PVOH, styrene acrylic saturation	1.1 to 2	Jopson 1993
Xytlan	Unrefined birch kraft, 25% PCC	Cationized birch xylan	1.2	Kataja-aho *et al.* 2012
Enzyme	Bl. HW kraft pulp, 450 mL CSF	Cellulose binding domains/ acrylamide graft	1.2	Kitaoka and Tanaka 2001
PEC	Peroxide bl. TMP & bl. SW kraft mix	APAM, CPAM, CMC	1.5 to 2.7	Kojonen *et al.* 2003
CMC	Spruce kraft pulp, ODED bleaching	Addition for CMC during O_2 delignification	1.17	Kontturi *et al.* 2008
Drying	Unbleached kraft, 20 ^{o}SR	Condebelt drying (linerboard weight, lab.)	1.3	Kunnas *et al.* 1993
Fibers	Bl. SW kraft, in fines, unrefined	Carboxymethylation, at same light scattering	1.8	Laine *et al.* 2003a
CMC	Bl. SW kraft, no fines, Na & Ca forms	CMC, varying DS & DP	2.5	Laine *et al.* 2002
Refining	Bl. SW kraft, no fines, Na & Ca forms	Refining (no CMC used)	5	Laine *et al.* 2002
CStarch	Various SW pulps (best effect bl. kraft)	Cationic aldehyde starch	1.1 to 1.9	Laleg & Pikulik 1993
Impulse	SW kraft pulp, 625 mL CSF, pressing	Impulse drying (STFI compression)	1.18	Larsson & Orloff 2001
PEM	Bl. virgin SW kraft fibers, unbeaten	PAH & PAA PEMs (5 individual PE layers)	2.2	Larsson & Wågberg 2008

Gum	SW sulfite pulp, 50 minutes beating	Locust bean gum as beater adhesive	4	Leech 1954
Fiber	Mixture of TMP and kraft	TEMPO oxidation of 5% of the pulp	1.2	Le Roux *et al.* 2006
PEM	Cellulose fibers	Lignosulfonate & cat. PAM layers	1.13	Li *et al.* 2012a
Cofloc	Filled, bl. euc. Kraft, 68 °SR, no fines	Coflocculation of filler and fines (pine)	1.06	Lin *et al.* 2010
PEC	Clay-filled paper	4.2% cationic starch & 0.3% anionic PAM	2.5	Lindström & Florén 1984
pH	Unbleached kraft pulp	Alkaline conditions	1.5	Lindström & Kolman 1982
PEM	Bl. SW kraft, Na form, unrefined	PE multilayers (8 total), lower molec. mass	2.7	Lingstrom & Wågberg 2008
PAM	Bl. SW kraft, 10 lb/ton alum	Dual treatment: aPAM & cat. poly & alum	1.4	Linke 1968
Enzyme	Unbleached SW kraft pulps	Laccase and wood-derived acids	1.06	Liu, Qin, & Li 2013
PEC	Redispersed copy paper, fibers only	PEC, *in-situ*, poly-DADMAC & CMC	1.36	Lofton *et al.* 2005
Enzyme	Unbl. SW kraft, 85 kappa, never dried	Laccase oxidation & heat curing	1.06	Lund & Felby 2001
Refining	Unused corrugated containers repulped	High consistency refining	1.05	Lundberg & de Ruvo 1978b
PEM	Bl. SW kraft unrefined	10% Wiley milled fibers PEM DADMAC/PSS	1.6	Lvov
Amines	Never-dried unbeaten spruce kraft	Polyallylamine, polyvinylamine masses	1.5	Marais & Wågberg 2012
Refining	Three unbleached kraft pulps	Refining had greater effect than pressing	2.8	Mathur *et al.* 1987
Refining	Pine unbleached kraft	Refining (PFI mill)	3.4	McKenzie 1964
Gels	Bl. SW kraft, unrefined from day-lap	Polyvinylamine microgels, linear, low XL	1.9	Miao *et al.* 2008
Lumen	Bl. spruce kraft, dry lab, cat polymer	TiO_2 lumen loading at pH 4, post polymer	1.3	Middleton & Scallan 1989
Oxidat.	Thermomechanical pulp (TMP)	Peroxide treatment of high yield pulp	1.4	Minor *et al.* 1993
Hemi	Rice straw extracted with 5.5% NaOH	30% treatment level with hemicellulose	6	Mobarak *et al.* 1973
DSA	Recyc. UBK linerboard, 0.01 N NaCl	Poly(allylamine hydrochloride) pH 7.5	1.2	Mocchiutti *et al.* 2011
CStarch	UBK linerboard dried, recycled	2% cat. starch before drying, reslurrying	1.2	Mocchiutti *et al.* 2006
Dual	90% solids bl. pine kraft, surf. fibrillated	Polysaccharides, esp. CMC & chitosan	2	Myllytie *et al.* 2009
PEC	430 mL CSF with alum	Pre-mix of cat. & an. PAM	1.3 to 1.5	Nagata 1991
Plies	Stiffness: 35% chem, 65% mechan. pulp	Optimized 3-ply board → highest stiffness	2	NavaeeA & Nazhad 2008
Refining	Old corrugated containers (OCC)	Optimized refining intensity & energy	1.44	Nazhad 2004
Dual	Waste pulp (burst strength)	Dual-polymer PAM system, alum	1.6	Nealey *et al.* 1989
Hemi	Reporting on work of Jonas & Rieth	Mannan, xylan, and both together	1.22	Obermanns 1936
Enz	Old corrugated containers (OCC)	Cellulose binding domains → strength	Up to 1.1	Pala *et al.* 2001
Refining	Corrugated container furnish	Refining to maximize ring crush, low intens.	2	Paulapuro & Thorp 1983
Starch	Bl. HW/SW kraft mixes	Blocked reactive group (BRG) starch	1.3 to 1.67	Peel 1989
Saturat	Bl. SW kraft pulps (saturation)	Molecular mass of dextran strength aids	1.35	Pelton *et al.* 2003
Spray	Old corrugated containers (OCC)	Starch spraying, paper machine trials	1.1 to 1.25	Proctor & Reid
Drying	High temp thermomechanical (HTMP)	Condebelt simulation, high initial moisture	3.3	Pynnönen *et al.* 2002

Ionic	Alpha cellulose, 325 mL CSF	Dye to fibers; polyamine sprayed on sheets	1.36	Reif 1972
Hemi	Old corrugated containers	Mod. hemicelluloses: cationic, anionic	1.2 to 1.7	Ren *et al.* 2009
Drying	European mixed waste	Condebelt drying	1.4	Retulainen 2003
PEC	Bleached pine kraft & spruce TMP	Cationic starch & CMC	1.8	Retulainen & N. 1996
Filler	Kaolin or whiting in printing paper	Filler pretreatment, agglomeration	1.26	Riddell *et al.* 1976
CStarch	Unbleached pine kraft, unbeaten	Cationic starch much better than native	1.6	Roberts *et al.* 1987
Fiber	Various sulfite, kraft pulps, unrefined	Carboxymethylation of pulp	2	Ruffini 1966
Coating	Calendered kraft paper, 100 g/m^2	Nanostructured coating or SMI particles	1.2 to 1.3	Samynn *et al.* 2010
PEC	Sulfite fibers, no fines, unrefined	Cat PVA with CMC	1.5	Sang *et al.* 2010
Hemi	Birch and spruce sulfite pulps	Cationic birch xylan	1.6	Schwikal *et al.* 2011
Decrill	Packaging paper (fixed freeness)	De-crilling of recovered fibers, refine to CSF	1.2	Selder *et al.* 2002
Filler	Ground CaCO$_3$, Bl. kraft 400 mL CSF	Preflocculation of GCC (17%) by CPAM	1.17	Seo *et al.* 2012
Refining	Bleached hardwood kraft (not SW)	Impact refining (*vs*. Valley beating)	1.3 to 1.4	Seo *et al.* 2000
Drying	Conventional drying, 8 diverse pulps	Press-drying to same apparent density	0.86 to 1.22	Seth *et al.* 1985
Fibers	*Corymbia citriodora* kraft pulp	Mature wood *vs.* juvenile wood (same SR)	1..1	Severo *et al.* 2013
Starch	Old newspaper (ONP), starch only	Potato starch, gelled by borax, ppt. on fiber	1.8	Shen *et al.* 2012
PEC	Unbleached board	Complex of polyamidoamine-epi & CMC	1.3	Smith 1992
Amphot	Bleached kraft sheets	Solution viscosity	1.5	Song *et al.* 2006
Hemi	Unbleached SW kraft	Carboxymethylated β-D-glucan	1.5	Song & Hubbe 2013
Hemi	Unbleached SW kraft	Tempo oxidation of β-D-glucan	1.36	Song & Hubbe 2014
Fiber	Aspen kraft pulp, virgin	Tempo oxidation of fibers	1.2	Song & Law 2010
Filler	10% kaolin clay or CaCO$_3$ filler content	Filler preflocculation	1.5 to 2	Stark *et al.* 1987
Fines	Southern unbleached pine kraft	Dry-strength agent on fibers, don't treat fines	1.1	Stratton 1989
Fines	Acrylamide dry-strength additive	Fines & location of dry-strength agent	1.7	Strazdins 1980
WSR	Salt-free conditions, dry strength	Polyamideamine-epichlorohydrin 10 mM salt	1.1	Su *et al.* 2012
Gums	SW sulfite pulp, 50 min beating	Locust bean gum as beater adhesive	1.3	Swanson 1950
MFC	Bl. SW kraft, refined to match drainage	MFC with fixatives for strength & drainage	1.3	Taipale *et al.* 2010
Enz	Virgin UBK, 445 mL CSF	Cellulases & hemicellulases, whole pulp	1.5	Taleb & Maximino 2007
CStarch	Refined kraft or mix of TMP and kraft	Cationic starch, up to 4% addition	1.2 to 1.7	Tanaka *et al.* 2001
Hemis	Bleached SW kraft, lightly beaten	Four hemicellulose fractions, bean gum	1.4 to 1.6	Thompson *et al.* 1953
Fiber	Paper strength, regenerated cellulose	Carboxymethylation of regenerated cell.	3	Torgnysdøtter & W. 2003

Fiber	Joint strength, regenerated cellulose	Cationic & anionic fibers helped by salt	3	Torgnysdøtter & W. 2004
PEM	Recycled kraft fibers	PEM PAH/PAA, rinsing, 5 layers	1.9	Torgnysdøtter & W. 2006
PEC	Old corrugated container (OCC) pulp	Cat. & anionic polyvinylamine	1.38	Truppner *et al.* 2006
Starch	Bl. spruce thermomechanical pulp, TMP	Cat. Starch derivatives, opt. charge density	1.1 to 1.9	Ulbrich *et al.* 2012
Drying	50/50 kraft/TMP sheets	Activation by tension during drying	1.15	Vainio & P. 2007a
Drying	Beating, starch, and fines, tensile mod.	Restrained drying (vs. unrestrained)	1.4	Vainio & P. 2007b
PECs	50:50 bl. pine kraft, bl. spruce TMP	PECs promote bonding despite drying stress	1.1	Vainio *et al.* 2006
PEM	Unbeaten & beaten bleached kraft	Cationic polyallylamine & anionic PAM	2.8	Wågberg *et al.* 2002
Fiber	Bleached rag cotton	Carboxymethylation of fibers	1.6	Waleka 1956
Saturat	Containerboard	Sodium silicate impregnation of paper	1.9	Walthy 1987
Refining	Old corrugated container (OCC)	Beating and pressing (combined)	1.34	Wan *et al.* 2011
CMC	Bl. HW kraft, 450 mL CSF	CMC adsorption with salt: Strength gains	1.04	Watanabe *et al.* 2004
CTMP	Thermomechanical pulp (TMP)	Sulfonation of TMP (CTMP)	2.5	Wegner 1982
PEC	Bl. birch kraft with 17% $CaCO_3$	Anionic starch with PAC fixative	1.6	Wielema & Brouwer 2003
Refining	De-inked TMP pulps, usual refining	Low consistency refining with low intensity	1.28	Wild 1998
Enzyme	High-kappa unbleached kraft pulp	Laccase mediated treatment	1.06	Wong *et al.* 2000
PEC	Old corrugated containers	Starch & poly-DADMAC	1.3	Wu, Chen, & Lu 2004
PAM	Bleached HW kraft, lightly beaten	PAM	1.7	Yamauchi & Hatan. 2002
Latex	Tensile: Comparing to weakest latex	Cat. crosslinking cationic latexes with epoxy	1.3	Yan *et al.* 2013
Filler	50:50 HW:SW bl. kraft, 400 mL CSF	Starch-treated clay; cooked together, ground	1.4	Yan *et al.* 2005
Enzyme	Bl. SW 550 mL & bl. HW 450 mL CSF	PAM coupled to cellulose binding domains	1.03 to 1.26	Yokota *et al.* 2009
DSA	Bl. SW kraft, unbeaten, deionized water	Cationic dextran charge density, hydrophob.	1.4	Zhang *et al.* 2000
DSA	Bl. SW kraft, unbeaten	Cationic dextran molecular mass	1.3	Zhang *et al.* 2001a
DSAs	Recycling of virgin unbleached SW kraft	Various dry-strength agents, cat. starches	1.1 to 1.6	Zhang *et al.* 2002
Filler	12% PCC in 65% TMP – 35% ONP pulp	Starch modification of calcium carbonate	1.6	Zhao *et al.* 2005

Key to Table A

APAM	Anionic copolymer of acrylamide
Bl.	Bleached
Cat.	Cationic (positive charge)
CD	Cross-directional (not in manufacturing direction)
CEH	Bleaching sequence: chlorine, NaOH, hypochlorite
CMC	Carboxymethylcellulose (anionic polymer)
CPAM	Cationic copolymer of acrylamide
CSF	Canadian standard freeness
DADMAC	A high-charge cationic polyelectrolyte
HTMP	High-temperature mechanical pulp
HW	Hardwood
MFC	Microfibrillated cellulose
NSSC	Neutral sulfite semichemical pulp
OCC	Old corrugated container pulp
ODED	Bleaching sequence with oxygen bleaching
ONP	Old newspaper pulp
PAA	Polyacrylic acid
PAC	Polyaluminum chloride (oligomeric, cationic)
PAH	Polyallylamine hydrochloride (cationic polymer)
PAM	Polyacrylamide (family of water-soluble polymers)
PCC	Precipitated calcium carbonate (filler)
PE	Polyelectrolyte
PEC	Polyelectrolyte complex
PEI	Polyethyleneimine (highly cationic polymer)
PEM	Polyelectrolyte multilayer
PFI	Norwegian Forest Prod. Institute (refiner type)
PSS	Polystyrene sulfonate
PVA	Polyvinylamine (highly cationic polymer)
PVOH	Polyvinyl alcohol
SMI	Polystyrene-co-maleimide nanoparticles
SR	Schopper Riegler degrees of freeness
SW	Softwood
TEMPO	Oxidation treatment for cellulose
TMP	Thermomechanical pulp