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RESPONSES OF PAPER PROPERTIES TO CHANGES IN MOISTURE CONTENT AND TEMPERATURE

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ABSTRACT

During production, converting and usage, paper and board products may be exposed to environmental conditions of both constant and variable nature. As these paper and board products are ultimately composites of the natural polymers cellulose, hemicelluloses and lignin, they are, due to their hydrophilic nature and also to the existence of thermal transitions, highly influenced by the surrounding environment. The paper properties are accordingly affected by moisture and temperature and it is these changes of a physical nature that are discussed in this paper.

In this paper, an attempt is made to present a philosophy of how the total performance of paper products can be reduced to the question of how moisture and temperature interact with wood polymers on a molecular level. The multicomponent nature of the wood fibre and the consequences of the build up of dried-in stresses are particularly emphasised. Thus the sorptive properties of the wood polymers are described from the standpoint of molecular interaction and a plasticizing effect which reduces the glass transition temperatures of the wood polymers. The consequences that this softening have on mechanical properties and on hygroexpansivity are presented together with descriptions of the effect of drying stresses and the creep behaviour during moisture cycling.

Practical examples are given, discussing high temperature processes such as hot calendering, corrugating and press drying. Effects related to printing and converting operations, such as dimensional stability, surface roughening and linting are also commented on. Finally some ideas regarding future research are presented.

INTRODUCTION

Paper materials, like all natural polymers, are affected by changes in the environment i.e. moisture and temperature. In fact, all natural polymers are more or less hydrogen bonded and their properties are thus intimately regulated by the relative humidity, i.e. the moisture content, of the surrounding environment. This may in fact be a prerequisite for all living matter; the ability to adopt to the changing environment in a way most suitable for each living species. Thus, by their nature, paper materials unavoidably exhibit highly different properties under different environmental conditions. In most cases, these changes in properties are undesirable, as for instance dimensional changes in printing operations resulting in misregister of printing colours. The sensitivity of the polymer properties with regard especially to changes in moisture content is however also exploited in the making of paper products and may in fact be the reason why paper may be utilised in such a variety of applications. The sensitivity towards moisture and temperature may also be advantageously used in such special operations as hot calendering and in the press drying of paperboard.

In the following, the nature of the interaction of moisture and temperature on paper properties will be examined from a polymer physics point of view. The idea has been to present a philosophy based on the concept of wood polymer softening in order to interpret effects of moisture and temperature on paper performance. It is recognised that paper consists of wood fibres composed of semicrystalline cellulose in the form of fibrils in an amorphous matrix of hemicelluloses and lignin and it is postulated that the effects of moisture and temperature on paper properties can be traced to their effects on these constituent wood polymers. In relation to this conceptual model, paper performance is examined from its moisture sorptive characteristics through the action of the sorbed water as a plasticizer to its effect on mechanical and hygroexpansional properties. Special emphasis is given to drying stresses in the wood fibre and to the release of these by the action of moisture and temperature.

In this presentation, the discussion of the effects of moisture and temperature are exemplified with wood, wood fibres and paper, recognising that the qualitative effects on these materials are similar. Effects of the pulp quality of the paper are accordingly viewed from the viewpoint that differences are due to differences in the chemical composition of the wood fibre.

In order to illustrate the practical consequences of effects of temperature and humidity in relation to the softening concept, a few examples will be discussed concerning high temperature processes and printing and converting operations, where e.g. Xerox copiers are sources of heat while unconditioned printrooms are sources of moisture.

The wood fibre structure

The complex wood fibre structure with cellulose fibrils arranged at different angles to the fibre axis, see figure 1, evidently provides for high restricting forces on the wood fibre. This is one reason why the effects of moisture and temperature on the properties of the wood fibre and paper may deviate

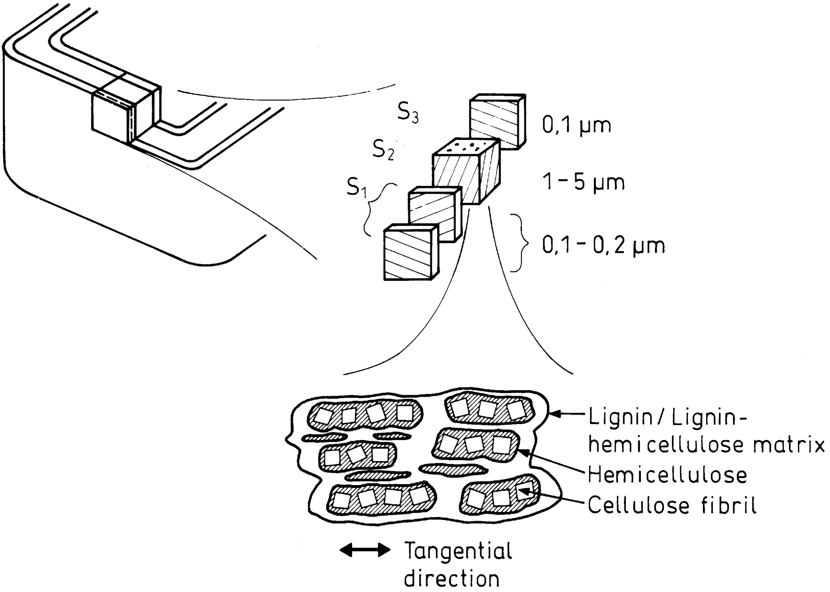

Figure 1 Schematic illustration of the structural build up of the cell wall of spruce fibres. For each cell wall layer S_1, S_2 and S_3, an average orientation of the cellulosic fibrils is indicated

considerably from their effects on homogeneous materials. Looking at the build up of fibres, it is evident that the S_2 layer will dominate properties since it makes up around 75% of the fibre wall volume, but the restrictive forces from the S_1 and S_3 layers must not be neglected (1).

In each of the cell wall layers, semicrystalline cellulose fibrils are arranged in parallel arrays at some angle to the fibre axis. These stiff fibrils are probably surrounded by some of the amorphous hemicelluloses while other hemicelluloses make up the matrix together with the amorphous, partly cross-linked lignin. The specific arrangement of these matrix polymers is still uncertain, whether they exist as separate components or as a homogeneous lamellar matrix (2). Mechanical studies indicate that the matrix hemicellulose and lignin act as separate components (3), although a close association, especially in pulp fibres, involving covalent bonding between hemicelluloses and lignin has also been shown (4).

The existence of disordered zones in the cellulose crystalline fibril is indicated by several investigations (see 5). If these disturbances disrupt the cellulose crystalline lattice, they have a profound influence on fibre properties (6), especially mechanical properties, as the cellulose fibrils act as the reinforcing component of the cell wall (1). The structural view here adopted, as illustrated in figure 2, depicts the cellulose fibril as being interrupted at more or less regular distances by zones of disturbed, "amorphous", cellulose surrounded by a matrix of hemicellulose with molecules preferentially arranged in the direction of the cellulose crystals (7).

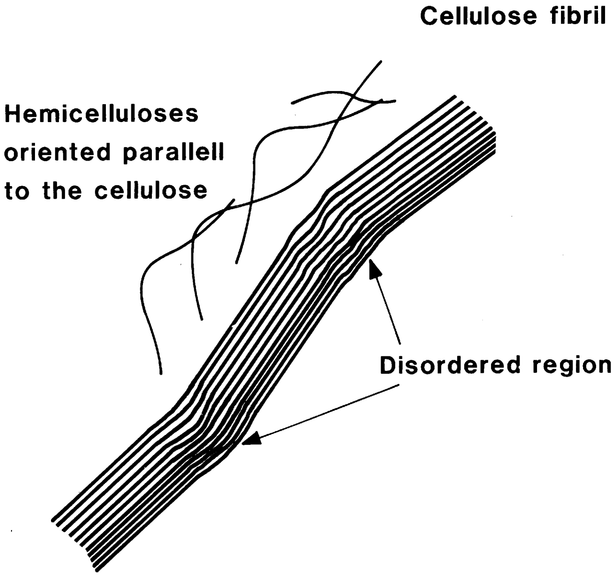

Figure 2 Schematic illustration of the structure of a cellulose fibril

An essential feature of this structure is the accessibility to water of these disordered zones (8) making it probable that they are associated with the softening phenomena.

In the following, the behaviour of the wood fibre and paper are examined in relation to this model.

SORPTION PHENOMENA

The hygroscopicity of the wood polymers is an essential characteristic of wood fibres and paper products and governs many of the properties exhibited by these materials. It is therefore of fundamental interest to have a deeper understanding of the interaction between water and the wood fibre material.

The sorption of water by the wood polymers and thus by paper follows the general behaviour of a hydrophilic polymer exhibiting a sigmoid sorption curve (9, 10), see figure 3. This sorption has been described with reference both to surface theories (12,13) and solution theories (14, 15) but neither of them is able fully to characterise the behaviour (9,16). When considering surface sorption theories, it should be pointed out that it is the surface of the wood polymers and not that of some macro- or microscopic cavity within the wood fibre which should be considered. One must also recognise that although water may be considered to be sorbed at a hydration site it may interact with other water molecules to form clusters (17) and that the energies of hydroxyl sites may vary depending on the proximity of neighbouring sorption sites (18). Thus water sorption is highly related to the molecular characteristics of the wood polymers. The sorption properties of wood fibre products may also be described by the sorption properties of the individual wood polymers, the hemicelluloses, the lignin and the cellulose (10), where it is generally considered that the amorphous or disordered

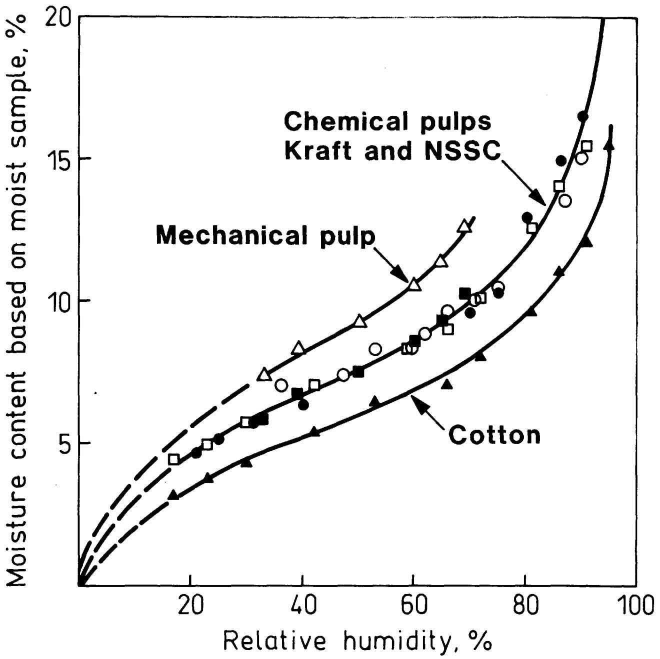

Figure 3 Sorption isotherms at 23°C in absorption for papers made from mechanical pulp, from chemical pulps and from cotton linters (11)

cellulose is sorbing water, the cellulose crystals having a negligible sorption capacity (19). This explains the lower water sorption capacity of cotton (pure cellulose), with its high crystallinity compared with that of wood fibres, see figure 3. Sorption should occur on hydroxyl sites of the cellulose crystal surface but this is a question of distinguishing between amorphous and crystalline cellulose. The hemicelluloses, due to their higher hydroxyl content, have a higher sorption capacity than the lignin. Mechanical pulps may nevertheless have a high moisture sorption per unit weight due to their relatively low overall proportion of crystalline cellulose.

As in the case of other hydrogen-bonding polymers, e.g. polyamides, the total number of water molecules sorbed at saturation should correlate with the number of hydroxyl groups present in the cellulosic material, indicating those sites as primary sorption sites (20). The bound water content, defined as water which may not crystallise when sorbed, reaches at saturation a value of about 0.35 g H_2O/g amorphous cellulose (21) which may be calculated to be close to one water molecule per hydroxyl site on the cellulose. Such a relation may however be only partly true for the wood fibre material as it has been shown that the number of carboxylic acid groups present natively in the wood fibre material in the hemicelluloses has an influence on the amount of water sorbed by the material, particularly at high humidities (21, 22). Furthermore the counterions to these carboxylic acid groups also influence the moisture sorption specifically at high humidities, so that more water is sorbed by the material in the sodium form than in the calcium form (21, 23), see figure 4. This difference in sorption is

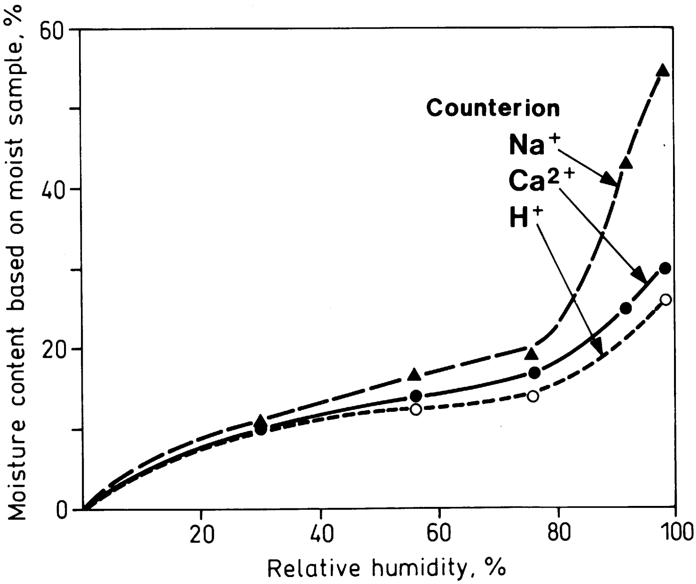

Figure 4 Sorption isotherms at 23°C for a carboxymethylated cellulose pulp (DS 0.29) in the ionic forms H^+, Na^+ and Ca^{2+} (22)

evident not only in the total water content at high humidities but also in the bound non-freezing water at these high humidities for a material containing ionic groups like carboxylic (from e.g. peroxide bleaching) or sulphonic acid (from sulphonation), see figure 5 (22, 24). Obviously the hydration volume of the counterions also influences the moisture sorption (24, 25). It is therefore probable that the sorbed water enters into the wood polymer material and is intimately mixed at the molecular level with the wood polymers, being sorbed on hydroxyl groups as well as on carboxylic and sulphonic acid groups but also forming, adjacent to the adsorbed sites, clusters which may move from site to site as well as hydration shells around ionic counterions.

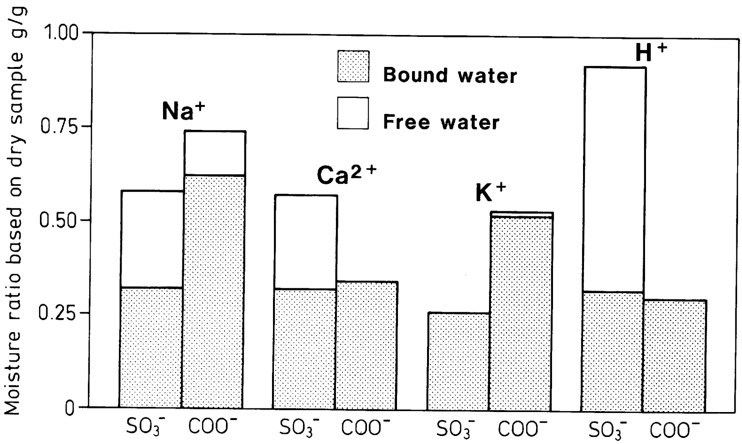

Figure 5 Amount of bound and free water at 92% RH for a carboxymethylated cellulose pulp (DS 0.29) and a sulphonated cellulose (DS 2.1) with different ionic forms. (22) The amount of the bound water was determined as the difference between the total water content and the free freezing water content as determined by DSC (Differential Scanning Calorimeter) (21)

It should also be recognised that there is generally a hysteresis effect in the absorption and desorption of moisture; a fact which has been associated with a viscoelastic (plastic) deformation of the wood fibre (26). This hysteresis tends to decrease with increasing temperature (27). The equilibrium moisture content is thus dependent on the pre-history of the paper or wood fibre material and is higher the higher the relative humidity from which the equilibrium situation is approached.

The equilibrium moisture content at a given relative humidity decreases with increasing temperature for wood materials (28, 29). At 100% RH, this decrease has been estimated to be 0.1%/°C rise in temperature and is due to thermodynamic effects. This fact further emphases the dynamic nature of the moisture - polymer interaction and that the sorbed water may not be tied to a specific sorption site.

Temperature changes in the environment thus change the properties of the wood material not only because of the absolute change in temperature but also because of the simultaneous change in moisture content of the wood fibre material.

The sorption of water also involves a heat release related mainly to the heat of condensation of the water vapour. This heat release can in extreme cases, in piles of insulating wood fibre products, be so large as to cause auto-ignition of the material (30). For free paper material where the diffusion of heat to the environment is much more rapid, temperature changes of 5-10°C may still occur, as exemplified in figure 6 (31, 32). Thus a moisture change causes a transient change in temperature which may also affect other properties before equilibrium values are reached.

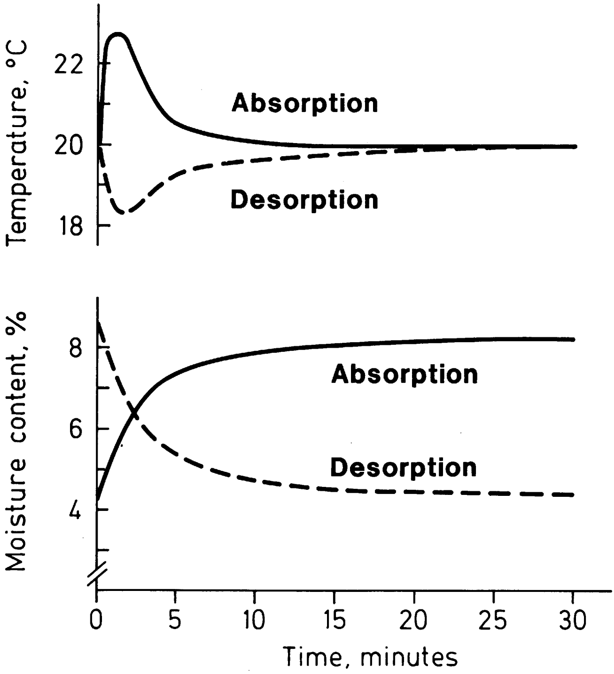

Figure 6 The temperature and moisture content as a function of time for a paper material absorbing moisture from 15 to 60% RH and the same paper desorbing moisture from 60 to 15% RH. The temperature was measured with a thin thermocouple placed between two papers of 105 g/m^2 (32)

Water uptake

When an excess of water is available, as in coating and printing operations or when the paper is used as an absorbent, water uptake will depend both on the structural arrangement of the fibre network and on the hygroscopicity of the fibres themselves (33). The pore sorption is of course dependent on the density of the paper product so the stiffness of the fibres and the long fibre content are of importance for an open network with a high water uptake. The hydrophobicity of the fibre surface is also essential. In the case of a sized paper, no water will be taken up by pores in the structure but only by sorption into the fibres themselves. Since it makes the fibre hydrophobic, the extractives content of the pulp is thus an important factor, especially for absorptive products based on mechanical pulps. At high levels of water uptake, when swelling becomes important, the water uptake is highly influenced by the amount of ionizable groups (carboxylic and sulphonic acid groups) in the fibre as well as by the particular counterion present (21, 22, 25), see figure 5. This is of importance for absorbent products.

In many industrial operations like gluing and printing, the wetting of the paper surface must take place during very short times and the phenomenon of a wetting delay of fractions of a second is important. The presence of extractives, which give the fibres a hydrophobic surface promoted by self sizing through ageing and temperature, leads to a prolongation of the wetting time (33). This wetting time is closely related to the matching of the surface free energy of the paper with the surface tension of the fluid (34).

WATER AS A SOFTENER

The moisture sorbed into the wood polymers is intimately mixed with these polymers and acts as a softener for them. The water interferes with the interaction forces, bonding, between the wood polymer chains and thus increases their mobility. A measure of these interaction forces between molecules is the cohesive energy density δ (35) which for lignin is about 22.5 $(J/cc)^{0.5}$ (36) and for cellulose and hemicelluloses has a value which has been reported to range between 32 and 52 $(J/cc)^{0.5}$ (37-39). In the cellulose and hemicelluloses, hydrogen bonds play an essential role in determining the interactive forces. Both these polymers have high values of the hydrogen bonding interaction parameter δ_h. This means that liquids

Solvent	Cohesive energy density $\delta(J/cc)^{0.5}$	Hydrogen bonding component $\delta_h(J/cc)^{0.5}$
water	47.9	34.2
formamide	39.3	19.0
glycerol	33.8	-
ethylene glycol	29.9	26.0
methanol	29.7	22.3
pyridine	21.9	5.9
dioxane	20.5	7.4
acetone	20.3	7.0

Table 1 Cohesive energy density for some substances (37) of interest with regard to wood polymers

with a high cohesive energy density and a high hydrogen bonding capacity interact most strongly with the wood polymers. The similarity of the interactive forces, i.e. that similar types of bonding mechanisms are involved, leads to better miscibility of the components, the polymer and its diluent. Water is one of the compounds with the highest known cohesive energy density, see table 1 (37), and it is therefore not surprising that water has such a large influence on the properties of the wood polymers.

For an amorphous or to some extent semicrystalline polymer, into which category the wood polymers fall, the glass transition temperature is the most characteristic parameter of the material. The glass transition temperature, T_g, defines the temperature at which the material changes its properties most drastically due to the sudden potential for large co-operative motion of the polymer chains, resulting in physical changes such as a substantial drop in elastic modulus, exemplified in figure 7 (about 3 decades for an amorphous polymer), increased expansivity and increased specific heat.

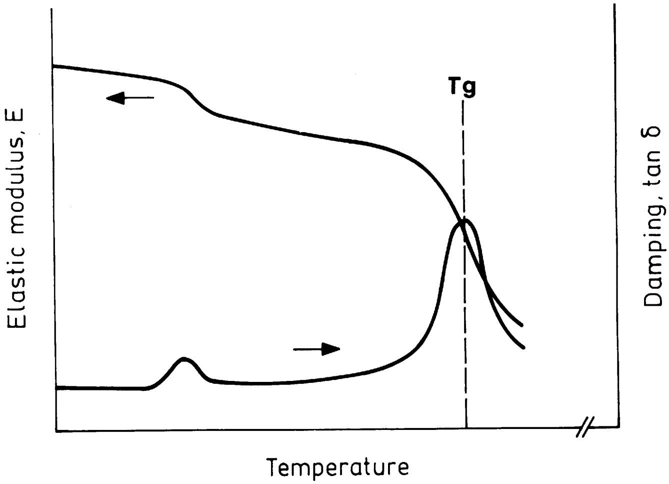

Figure 7 Schematic graphs of the elastic modulus, E, and the mechanical damping, tan δ for a material passing through a secondary transition and the glass transition T_g with increasing temperature

The term "softening" means that the glass transition temperature of the polymer is lowered with increasing amount of plasticizer. In the case of the wood polymers, this is for instance water. The softening points of hemicelluloses can be reduced from temperatures in the dry state of 160 to 200°C (41, 42) down to below 0°C at high moisture contents, see figure 8 (40). Although cellulose is similar in chemical structure to the hemicelluloses, the restrictions imposed on the amorphous or disordered parts by the crystalline regions of the cellulose mean that cellulose under dry conditions has a glass transition temperature of about 230°C (41, 42), i.e. higher than those of the hemicelluloses. Also, more water is needed to lower this temperature, meaning that the disordered, amorphous cellulose probably only softens at room temperature at moisture contents reaching about 50%, as indicated by dynamic mechanical studies of the drying of paper (43).

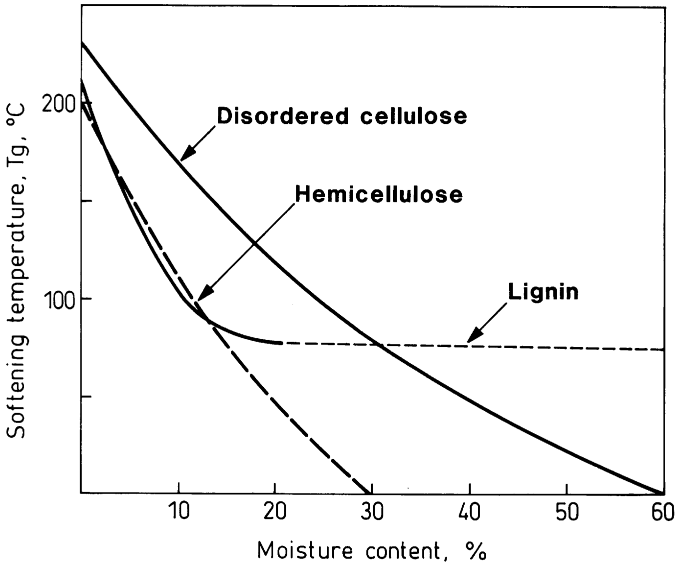

Figure 8 Schematic picture of the glass transition temperature for lignin, hemicelluloses and amorphous cellulose as a function of moisture content, based on experimental data and theoretical calculations (40)

In the case of lignin, there are also restrictions due to the presence of cross-links, which means that this polymer has rather a high glass transition temperature of 205°C when dry (41, 42). The restrictions also mean that only a limited amount of water may be sorbed by the lignin and thus a limiting transition temperature at water saturation is reached at about 90°C for a frequency of 1 Hz (44). In pulped fibres, the lignin glass transition temperature T_g may be altered due to structural changes in the lignin. During pulping, the kraft fibre is highly swollen due to high alkalinity, and this results in a considerably lower T_g of the modified lignin (45). However, the washed pulp has an even higher T_g than that of native lignin (45), which means that for paper, both of mechanical and chemical pulps, under normal operating conditions i.e. in use between 30 and 80% RH, it is only the softening of the hemicelluloses that affects the properties. However, for papers of mechanical pulps, the softening of the lignin at higher temperatures is of importance, just as the softening of the disordered cellulose plays a predominant role for all papers under very moist conditions.

PHYSICAL PROPERTIES

Thermal effects

The changes on the molecular level brought about by the changes in temperature and moisture content naturally influence the physical properties of the wood fibre and paper materials. With increasing temperature, the molecular mobility of the wood polymers increases, leading to an expansion of the solid and also resulting in a gradual diminishing of the elastic modulus (46, 47). These effects have been related to thermal effects on the hydrogen bonds in the cellulose solids (47, 48) and the calculated effect agrees with the experimental data of figure 9, which shows the modulus decrease dlnE/dT between 2 and 3.8 · 10^3/°C (40, 48). The differences between pulps may be related to differences in the amount of crystalline cellulose, which is less affected by temperature than the amorphous component (40).

At the softening temperatures of the wood polymers, the molecular mobility increases drastically leading to a higher thermal expansivity but more importantly it leads to a drastic reduction in the elastic properties (46), see figure 9. This softening also results in an expected substantially increased elongation and a decrease in strength properties (46). However, already at 150° degradation of the wood occurs and this accelerates at higher temperatures (49).

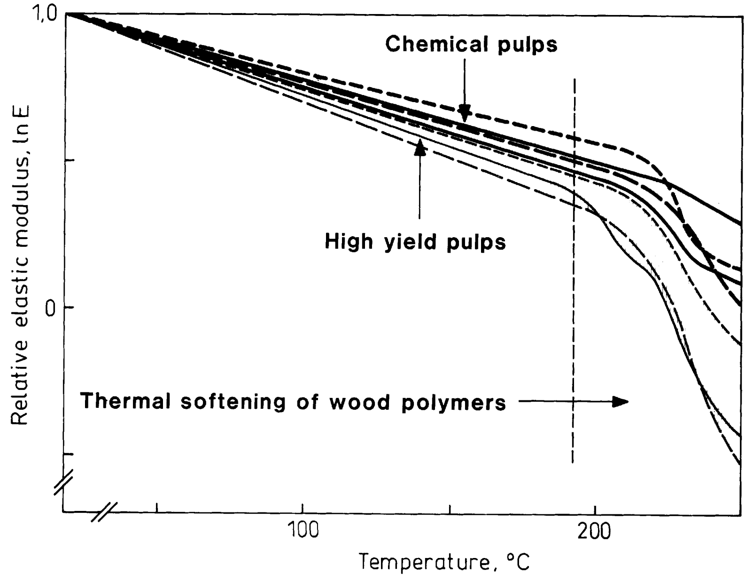

Figure 9 The relative elastic modulus of dry papers as a function of temperature (46). Above ca 190°C all the wood polymers, hemicelluloses, amorphous cellulose and lignin, soften which results in a substantial reduction in the elastic modulus

Wood fibre swelling - hygroexpansion

Moisture uptake in itself means that volume is added to the wood polymer system, i.e. that an expansion of the solid takes place (9). At very low moisture uptakes, the added volume is somewhat smaller than that of the added water i.e. there is a specific volume contraction (50), but above ca 7% moisture content, for paper, the added volume matches that of the added free water. For inhomogeneous wood or paper the expansion depends on the pore volume i.e. on the density of the material. In principle, swelling of the wood fibre could take place into the cell lumen,

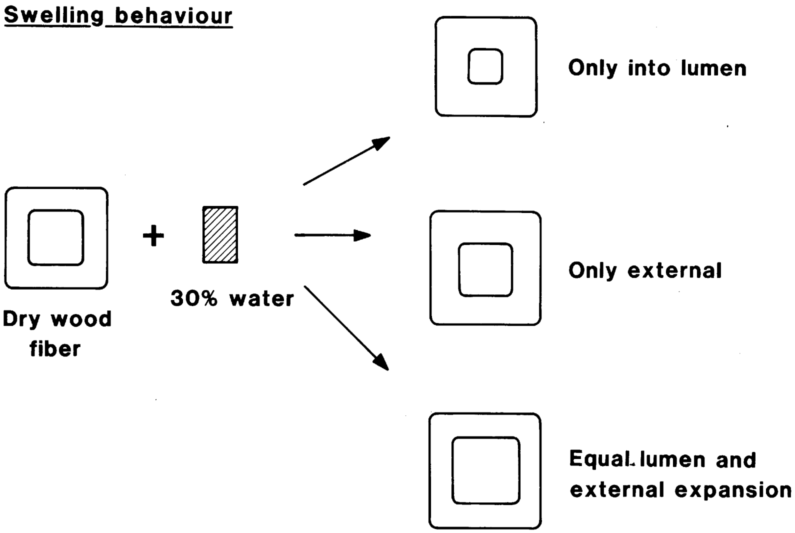

Figure 10 Schematic illustration of the volumetric swelling of a wood fibre cross section from its dry condition to fibre saturation, adopted after Tiemann (51). The swelling in the longitudinal fibre direction is negligible. The areas indicated for the fibres represent the actual swelling

the lumen volume could remain constant, or the cell lumen could expand to the same extent as the cell wall itself (51, 52), see figure 10. In general terms, wood fibres and wood swell in such a way that the pore volume remains approximately constant (53), which means that the volume expansivity is higher the higher the density of the wood (53), see figure 11. Although pores in papers are mostly due to cavities between fibres, a similar behaviour with regard to density has been indicated (52), presumably because the cross fibre expansion pushes fibres apart in the thickness direction. In the case of the wood fibre, this behaviour is presumably due to the build-up of the fibre wall, figure 1, and the

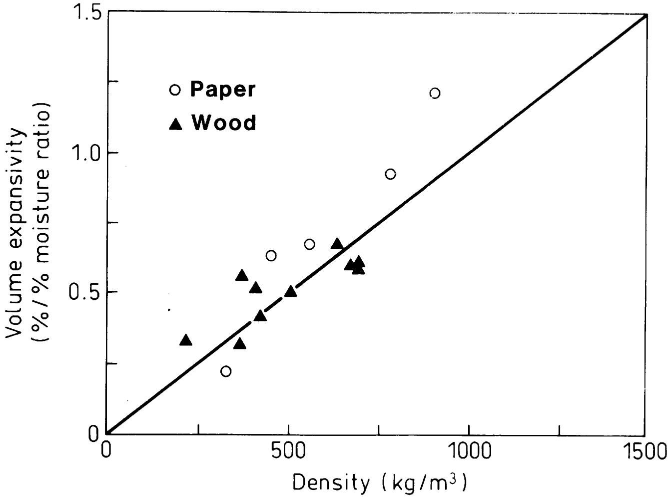

Figure 11 Volumetric expansivity of different wood species and of various papers as a function of density [data for paper (52), for wood (54)]. The line represents expansion of the material with no change in the lumen or pore volume

restrictions this imposes on the expansion. In the longitudinal fibre direction, thermal expansion or hygroexpansion is normally marginal (54) so that the expansion occurs in the cross fibre direction. However with the high fibril angle of the S_3-layer, the cell wall, although thin, will restrain swelling into the lumen (9). Buckling of the S_3 wall must then occur if swelling is to occur into the lumen. Swelling into the lumen is thus only observed when very high stresses can be built up, as in highly swellable holocellulose fibres with intact S_1 layer (55).

The hygroexpansivity, which is associated directly with the moisture uptake, is probably mainly associated with the hemicelluloses, as water is dominantly sorbed by these (9, 10). As the cellulose fibrils hinder the expansion of the hemicelluloses along the fibril axis, and thus along the fibre, figure 1, hygroexpansion in the case of fibres with a normal fibril angle of the S_2 layer i.e. a fibril angle between 0 and 40°, is predominantly in the cross fibre direction (56), and in the case of paper in the out-of-plane direction (52).

Moisture - elasticity

Due to the swelling of the wood polymer system as water is sorbed, the stiffness of the material diminishes. As moisture acts as a plasticizer, the mechanical properties are particularly affected in the vicinity of the glass transition temperatures of the wood components and depend on how this softening temperature is lowered with the addition of water (57). This is particularly evident under warm humid conditions when the paper stiffness may be reduced to such an extent that the paper may be difficult to handle.

The structural arrangement of the wood constituents is such that the stiff cellulose fibrils act as reinforcements in the wood fibre and thus largely determine the elastic properties of the fibre in its longitudinal direction, see figure 1. However, because of the high fibril angle of the fibrils in the S_1 and S_3 layers, the cellulose fibrils also influence the cross fibre properties (1, 40). The hemicelluloses may be considered to be arranged between the cellulose fibrils in a parallel array with them. It is therefore not surprising that the softening of the hemicelluloses occurring below 80% RH and amounting to a modulus reduction of about 3 decades (58) leads to a decrease of only 10 - 20 % in the fibre longitudinal modulus (40, 59). On the other hand, at very high moisture contents, the fibre modulus is reduced by more than 50% (somewhat more in torsion) (40, 60) see figure 12, a fact that may be attributed to the softening of the disordered zones of the cellulose. This softening affects fibre properties in an aqueous suspension and is for instance relevant for the situation in the wet pressing operation on the paper machine.

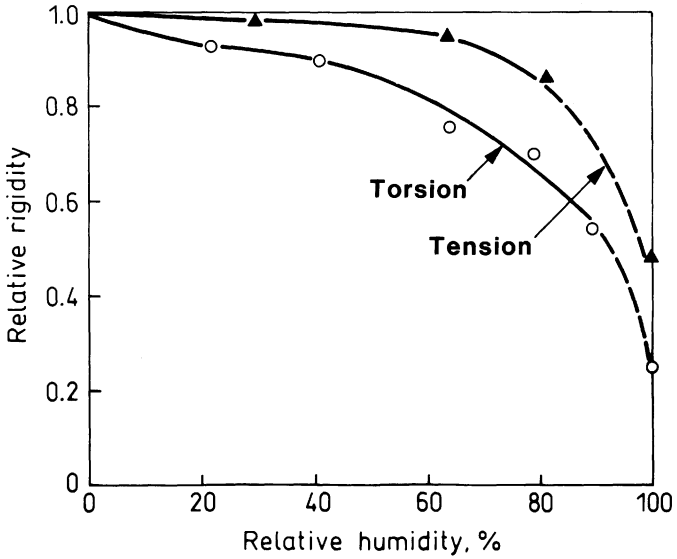

Figure 12 The relative rigidity of fibres tested in tension (59) and in torsion (60) as a function of the relative humidity. Up to 80% RH, softening of hemicelluloses occurs; above this humidity softening of disordered cellulose takes place

From the structure of the fibre it is clear that the effects of moisture on the fibre elastic modulus are reflections of the parallel coupled system of the cellulose and the hemicelluloses, which minimises the effect of the hemicellulose softening. On the other hand, the series coupling of disordered zones in the cellulose fibres makes the system very sensitive to moduli changes in these zones as is schematically illustrated by the calculations in figure 13.

Consideration of the reinforcing structure of the cellulose makes it clear that the effects of moisture should be directionally dependent, as is illustrated in figure 14 both for wood and for paper (61-63).

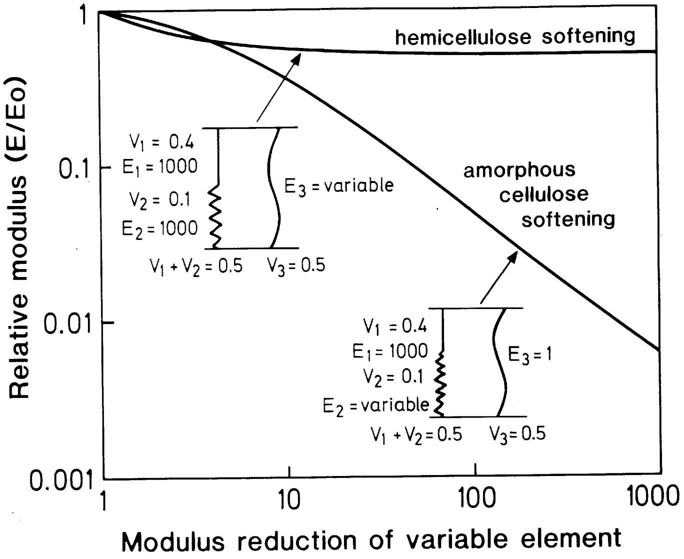

Figure 13 Model calculation of the relative elastic modulus of a wood fibre wall as a function of a softening of either disordered cellulose zones, E_2 or hemicelluloses, E_3. The disordered zones amount to 20%, $V_2/(V_1+V_2)$ of the cellulose and the hemicellulose content to 50%, V_3. Moduli values are relative and taken as reasonable for polymers passing a glass transition

As the orientation of fibres in paper is not as accentuated as in wood, the difference between the two directions of the paper is smaller. However, the fact that the moduli values for paper fall below those of wood even for the cross-grain values may indicate that the fibres in paper are more sensitive to property changes in the hemicelluloses, possibly because of disturbed structures in the pulp fibre such as kinks and microcompressions, these being regions where the cellulose reinforcement has a smaller effect. The variation in effects of moisture on the properties in the two directions is presumably due to variations in the fibril angle of the S_2 layer of the samples tested (64).

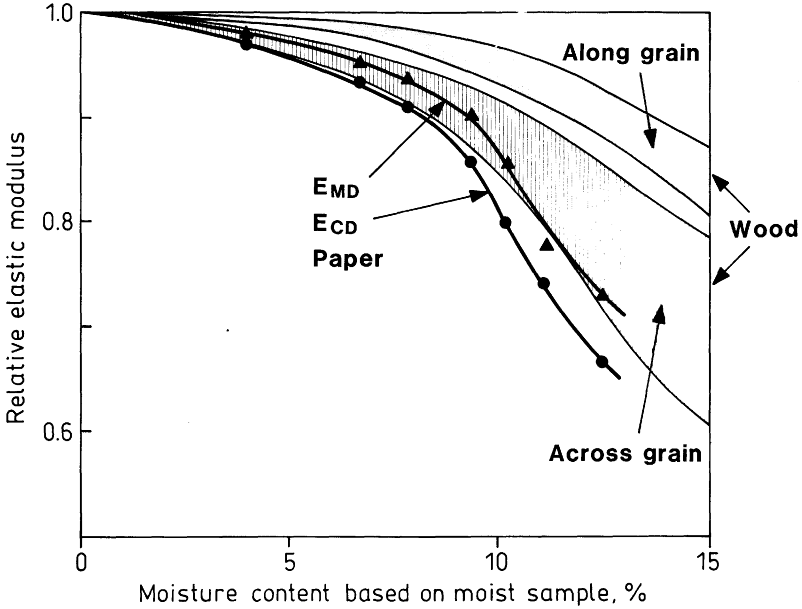

Figure 14 The relative elastic modulus as a function of moisture content for wood (61, 62) in the fibre direction (along grain) and across fibres (across grain) as well as for a laboratory paper of bleached sulphate pulp in the two principal directions (63)

As indicated earlier, moisture and temperature are to some extent interchangeable in their effects on paper properties. Property changes which are affected by the shift of the softening point with temperature are illustrated by the elastic modulus data in figure 15 (57). The softening region is clearly very broad, which is not surprising for such a complex composite system as the wood fibre. It is clear that an increase in temperature shifts the softening region to lower moisture contents in accordance with the general behaviour of plasticized polymers. These effects of water have been described by Nissan et al. (47, 48) as an effect

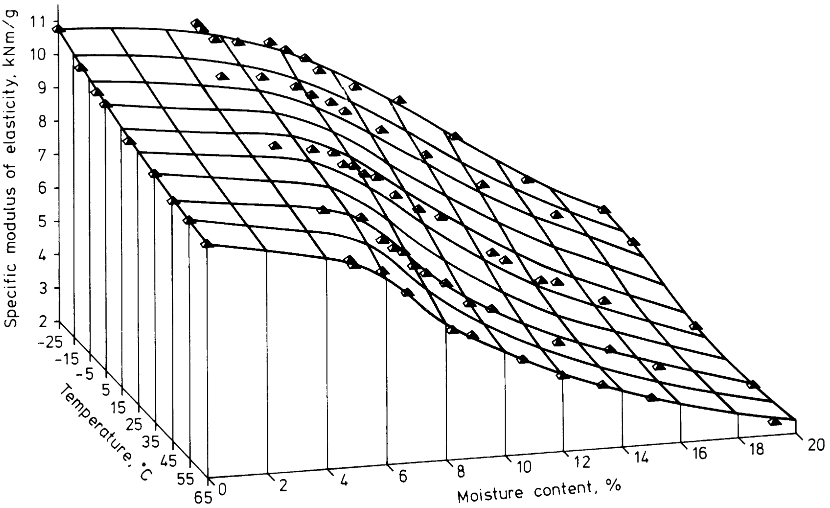

Figure 15 Specific elastic modulus as a function of temperature and moisture content for a kraft sack paper (57)

on the hydrogen bonds in the cellulose system, the more pronounced effect of water at higher moisture contents being attributed to a co-operative breakage of the hydrogen bonds. The physical relevance of a change in the critical moisture content where co-operative breakage occurs with increasing temperature has also been demonstrated (65). In principal, this view of the effect of water is clearly compatible with the plasticizing, in view of the high hydrogen bonding interaction parameter of this system. It should here also be pointed out that although moduli values differ depending on whether paper is conditioned from a higher or a lower moisture content there is no difference in properties when these are related to the actual moisture content of the paper (57). It is the interaction of the moisture present within the wood fibre that affects the molecular properties of the wood polymers and thus determine the properties of the paper. Of course, the softening effect of moisture and temperature affects all the

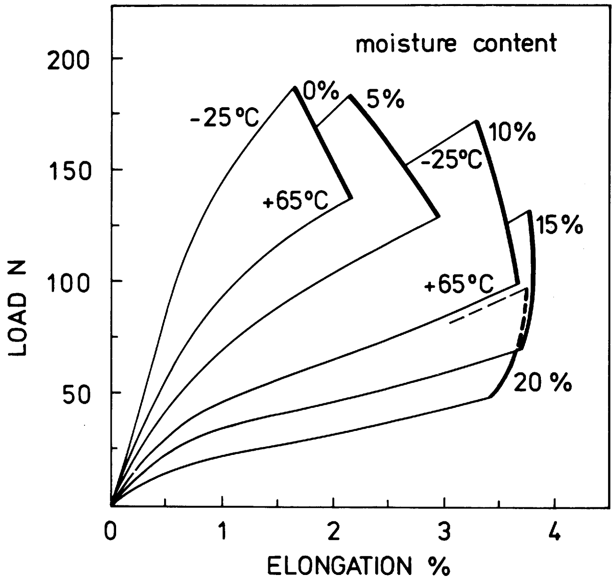

Figure 16 Failure envelopes for a kraft sack paper in the machine direction at temperatures from -25 to 65°C and moisture contents of 0, 5, 10, 15 and 20%, based on moist paper. Strain rate = 0.83%/s (57)

mechanical properties in a typical manner as illustrated in figure 16; tensile (57) and compression (66) strength decrease, elongation increases (57) and creep increases (67). The decrease in strength is similar in magnitude to that of the elastic modulus and is somewhat greater in compression than in tension (66, 68, 69), possibly due to the instabilities of the disordered zones which may initiate failure in compression (66).

Although lignin is to some extent cross-linked, which should mean that its modulus is reduced somewhat less than that of ordinary amorphous polymers when it is softened, its effect on fibre elasticity is substantial (40, 70). This may indicate a lamella type of organisation of the lignin, i.e. the lignin matrix is not restricted to such a large extent by the cellulose reinforcement as is the hemicellulose. However, due to the complex structural arrangement of the cell wall, neither the amount of lignin nor that of hemicelluloses has any marked influence on the degree of softening (40, 71).

At low moisture or softener content, when the lignin softens at about the same temperature as that of the hemicelluloses, see figure 8, a much larger modulus reduction is evident in lignin-rich materials (70). This occurs under conditions at which for instance hot calendering takes place. Under very moist conditions when both the hemicelluloses and the disordered cellulose are softened, the lignin softening is critical for the mechanical properties of the wood fibre; a situation of importance in the refining of mechanical pulps, i. e. moisture-saturated conditions at or above 100°C (44). In the case of the elastic modulus, this lignin softening - as is true of the hemicellulose softening - is more important across than along the fibre direction due to the restrictions brought about by the cellulose fibrils along the fibre direction (40).

Effects of drying restraints

For polymeric materials in general, the mechanical properties are to a great degree affected by any mechanical restrictions imposed on the material as it passes the softening temperature. Drawing of the material or hindering its natural shrinkage, for example, will orient the molecules in the direction of the stress (72). In the manufacture of paper, restrictions during the drying are common practice. The drying presumably takes the paper material through the softening point of the disordered cellulose at about 50% solids content (43) as well as through that of the hemicelluloses at about 80% solids content (58), see figure 8. Restrictions imposed by the paper machine draw during the drying operation affect both the elastic modulus and the hygroexpansivity of the paper. This restricting effect of machine

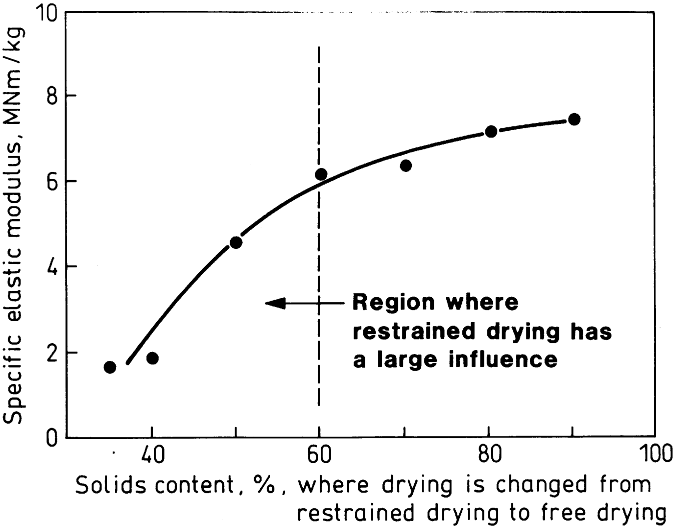

Figure 17 The elastic modulus of papers obtained by drying them under full restraint up to a specified solids content given on the abscissa and then letting them dry freely to full dryness. The paper has to be dried under restraint in the region below 60% solids content in order to achieve a high modulus of the paper; adapted after Htun (73)

draw is used in order to obtain high stiffness of the paper product, as in liner, and also when drying papers freely, as with sack paper, in order to achieve high tensile energy absorption (73).

The elastic modulus is affected by shrinkage restrictions mainly at low solids contents, i.e. under conditions in the vicinity of the presumed softening of the disordered cellulose zones (73), figure 17. This is a reflection of the fact that it is the cellulose fibrils that primarily determine the elastic properties of the wood fibre. If, for example, the cellulose disordered zones are oriented in the fibre direction by the applied stress,

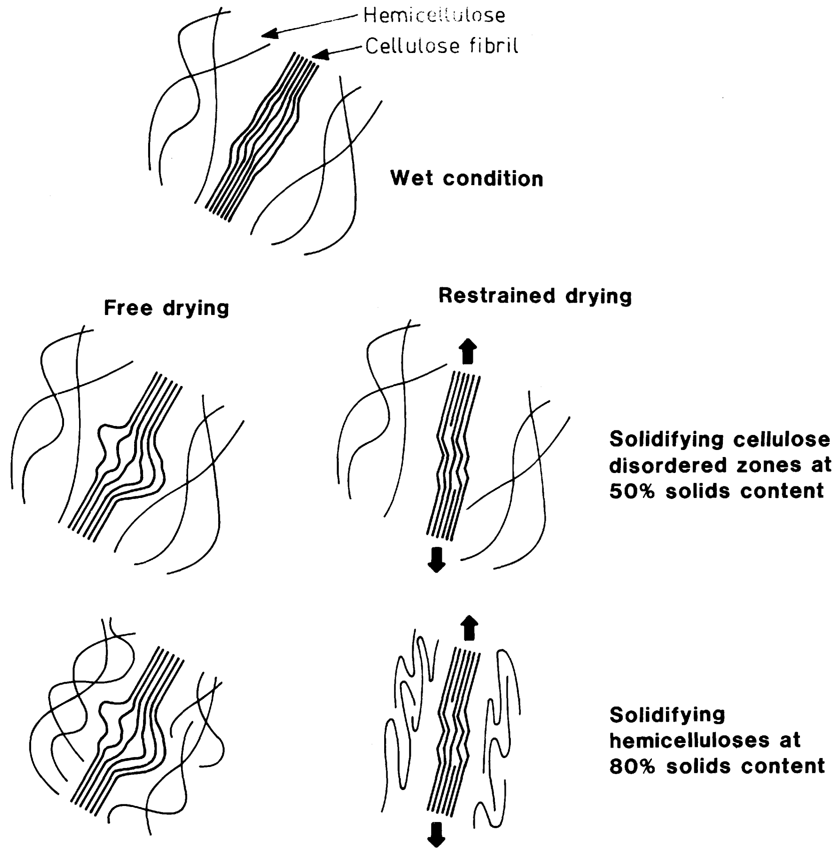

Figure 18 Schematic picure of the changes in the structural arrangement of the disordered cellulose zones and the orientation of hemicelluloses during drying

see figure 18, and then held in this condition by the lowered mobility as the moisture content decreases, the elastic modulus of the fibre is increased in the longitudinal direction and that of paper in the direction of the draw (74).

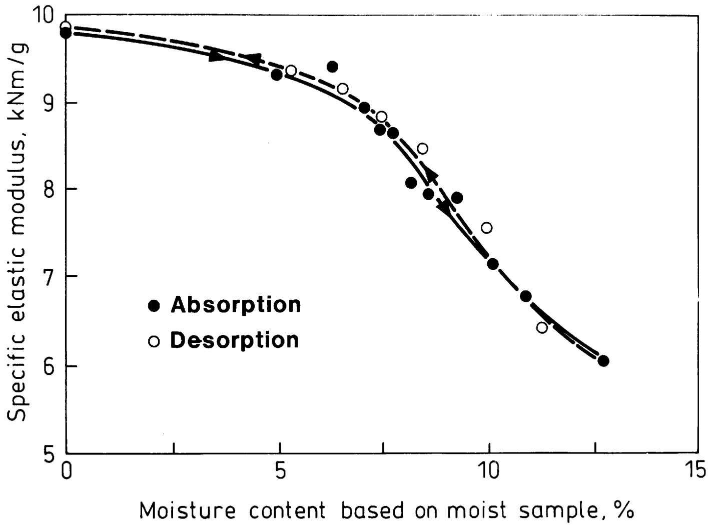

Figure 19 The specific elastic modulus of a kraft paper as a function of moisture content during both absorption and desorption of moisture (23, 57)

This gives the paper a higher stiffness in the machine direction without seemingly affecting the cross-machine properties (75). At lower moisture contents, when hemicelluloses solidify, they also may be oriented by restrictions. However, as the disordered cellulose zones are already solidified, the cellulose will counteract drawing stresses in the fibril direction., see figure 18. The orientation of the hemicellulose chains may thus, depending on the fact that fibrils are always laid at an angle to the fibre axis, have more influence in the cross-fibre direction.

It is also evident that, although the modulus in the longitudinal fibre direction is reduced somewhat by hemicellulose softening, no dried-in stresses are released when the humidity of the environment is increased to about 75%. When dried again freely, the paper regains its moduli at the drier condition (23, 57, 74), figure 19. The modulus increase in the

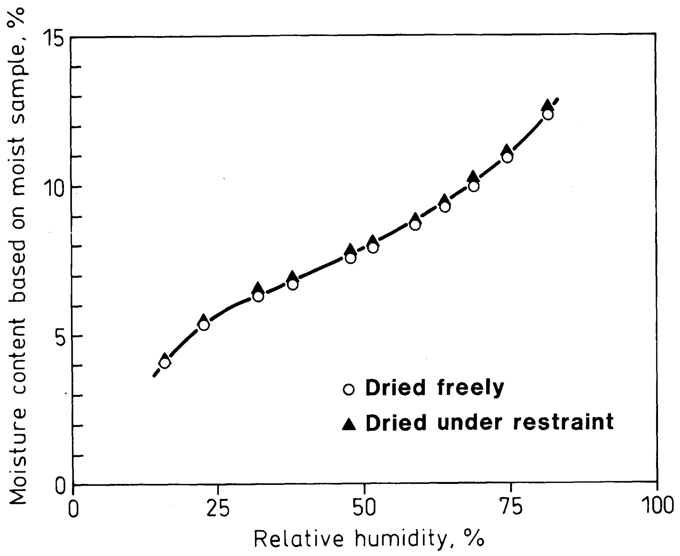

Figure 20 Moisture sorption isotherm at 23°C for sheets dried either freely or under restraint; moisture content based on moist sample weight (77)

longitudinal direction achieved by restraining of the hemicelluloses is thus so small in comparison with the modulus of the cellulose that its effect is negligible. Similar results have been found in the case of the compression strength, which was found to be unaffected by moisture cycling between 0 and 90% RH (66).

The application of a restraint, although aligning the molecules, has no effect on the moisture sorption, as is shown in figure 20, although tension as such has been reported to increase the moisture content of paper slightly (76). Obviously, the aligning of molecules does not affect the accessibility to their hydration sites and the sorption is therefore unaffected.

In contrast to the elastic modulus, the hygroexpansivity is highly influenced by restrictions affecting the orientation of both the cellulose and the hemicelluloses chains (74). As hygroexpansion mostly reflects the moisture uptake by the hemicelluloses, it is not surprising that restrictions, i.e. orientations of the hemicellulose, affect the hygroexpansivity. The hygroexpansivity is however also affected in other directions, in keeping with a more or less unaffected volumetric hygroexpansivity (if irreversible effects are neglected). It is only the directional dependence that may be affected, i.e., if the in-plane hygroexpansivities are reduced, the out-of-plane hygroexpansivity increases (52, 77). This implies that the moisture uptake is not affected by the restrictions imposed on the material during drying. These effects of restrictions are easily released when the softening point of the polymer is approached or exceeded. Thus, merely by increasing the relative humidity to about 50-60%, dried-in stresses in hemicelluloses can be released, thus increasing the hygroexpansivity of the paper if it has been dried under restraint to very low relative humidities, see figure 21.

In the case of lignin, restrictions leading to stresses in this polymer must be applied at high temperature, 75-80°C even when wet, as this is the softening temperature of lignin under moist conditions (44). Phenomena such as latency removal in mechanical pulps may be associated with dried-in stresses in lignin (78). To some extent, the high stiffness of fluting made of NSSC-pulp where the lignin is sulphonated and thus has a lower softening temperature than that of native lignin may be a reflection of dried-in stresses restricting the lignin as the fluting is moulded in the corrugating process.

Non-equilibrium environmental conditions

The effect of a changing environment on their mechanical properties is particularly troublesome for load-bearing products, as the mechanical properties are affected by the change to a greater extent than would be anticipated from measurements of the properties under equilibrium

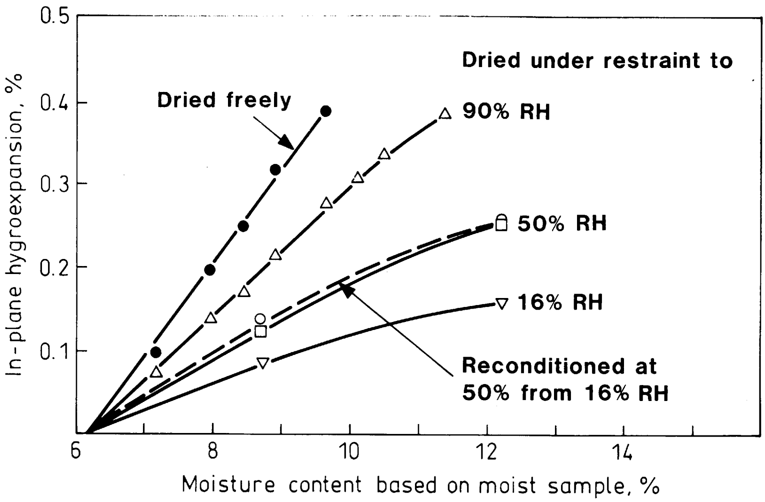

Figure 21 The in-plane hygroexpansion as a function of moisture content for sheets dried freely or under restraint down to different RH-levels and, in one case, reconditioned at a higher RH (23, 74)

conditions (79). The result is a much higher creep rate under cyclic conditions than at a constant high humidity, see figure 22, which may in the long run lead to failure of the product. The mechanisms behind this phenomenon, referred to as mechano-sorptive effects, are highly debated and have definitely not been fully solved.

Transient effects have been observed during sorption, where for example the elastic modulus has been observed to fall below the value associated with the highest experienced humidity (79), but these observations may only be due to deficiencies in the experimental technique of measuring properties under changing conditions (31, 32).

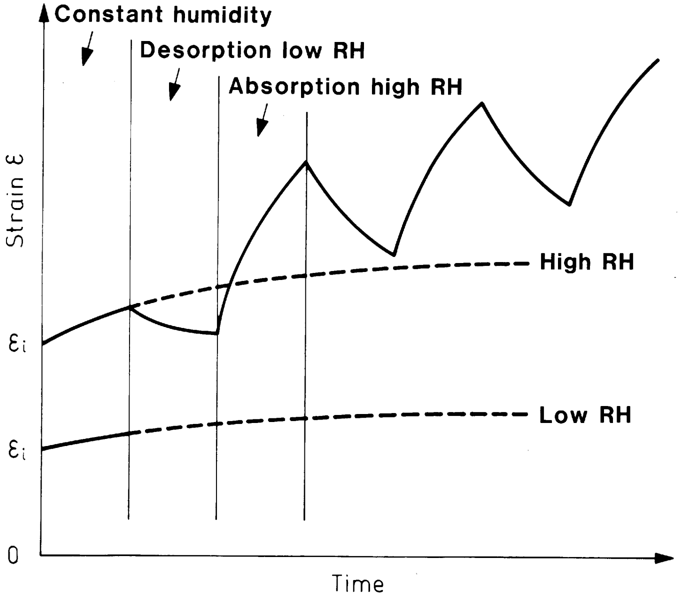

Figure 22 Schematic diagram of tensile creep under constant and cyclic humidity conditions. The initial strain ε_i is associated with the load applied to the sample

The fact that mechano-sorptive effects are most pronounced in compression (77) has led to hypotheses regarding the development of dislocations in the fibre structure which should lead to greater hygroexpansion and lower stiffness (80, 81). It has also been observed experimentally in the bending of corrugated board (81), that the hygroexpansion is higher in compression and lower in tension than when no stress is applied. Mechano-sorptive effects occur almost only in complex structural materials, where dried-in stresses may develop between components during the solidification of the material. When the humidity is increased in such a material, the dried-in stresses are likely to be released.

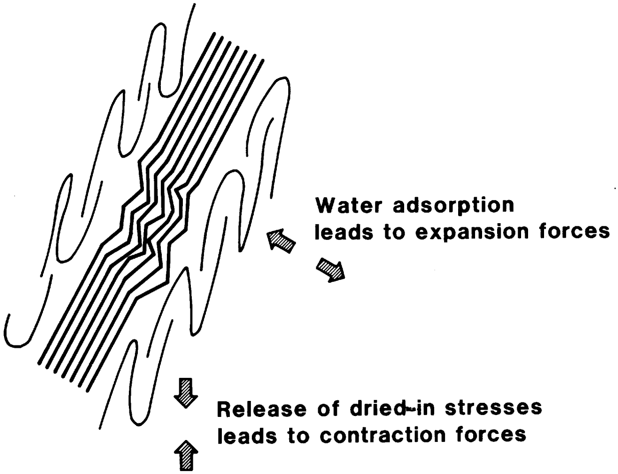

Figure 23 Schematic picture of the release of drying stresses affecting elastic properties under tension or compression

In a material containing dried-in stresses, the molecules are extended in the direction of the applied drying stresses. When the moisture content is increased and the molecular mobility increases, these stretched molecules desire to contract. If tensional forces are acting on the sample, the molecular contraction will be hindered, but the desire of the molecules to contract represents a contraction force which counteracts the tensional forces on the sample, see figure 23. In essence this means that the sample has a lower hygroexpansion under tension. On the other hand, under compressive forces the molecules experience less resistance towards contraction. Thus, due to the stress release, the elastic modulus of the material is lowered and the net hygroexpansion increases.

It has also been suggested that physical ageing - de-ageing should lead to mechano-sorptive effects (82). The increase in moisture content moving the material close to or above its glass transition causes de-ageing, i.e. increases the molecular mobility and the free volume of the polymer, a phenomenon similar to that of releasing dried-in stresses. However, the effects occurring as a direct result of the release of dried-in stresses should be more pronounced than those due to a pure de-ageing of the material.

The greater the magnitude of change in relative humidity the larger is the mechano-sorptive creep (83). With a larger humidity change, a higher moisture content is reached than if the sample is exposed to several smaller RH steps (84). The sorption of water also occurs relatively more rapidly if the change in relative humidity is large (84). It may be that, with more non-bonded water present with a larger moisture gradient, stresses may be released to a greater extent than if the moisture increase occurs in small intervals. With a constant moisture gradient through the sample, i.e. when there is a flow of water molecules through the sample, no mechano-sorptive effects are observable (85, 86). In this case, water molecules associated with the hydroxyl groups of the wood polymers may be more stationary, only those having a lower bonding energy moving through the sample without interacting with the more bonded water. This could leave the wood polymers unaffected or at least not give them any greater freedom of movement, since no exchange of water molecules would occur.

With water as the interacting medium, it is noteworthy that mechano-sorptive effects seem to occur only in complex hydrogen-bonded systems such as, besides wood fibres, wool (85) and aramide fibres (88). Mechano-sorption is therefore very probably an interactive phenomenon in which stressed bonds in the system are released by the medium (88). Thus, it is highly probable that the mechano-sorption is related to an increased mobility of the molecules (79).

PRACTICAL EXAMPLES

In the previous sections, an attempt has been made to establish that the effect of moisture and temperature can be traced to an interaction on a molecular level with the individual wood polymers. It has also been suggested that dried-in-stresses have a great influence on the properties as a consequence of the multicomponent nature of the wood fibre. In the following, some practical examples of consequences relating to product performance are discussed.

Effects in high temperatures processes

Calendering

High temperature soft-nip calendering is a prime example where the environmental properties of paper have been utilised to yield the most beneficial surface properties (89-92). With increasing temperature, the wood polymers of the paper are plasticized. Using a calender with very hot surfaces, a temperature gradient will develop between these surfaces, those of the entering paper web and its centre. Due to the higher compressibility of the softer outer surfaces, these will be more densified than the bulk of the paper web and thus a paper with high gloss but with a comparably high bulk will be produced (90).

A similar effect may be obtained by moisture gradient calendering, in which the surface of the paper web is moistened prior to passage through the calendering nip (93). The water, not having had time to soak into the paper, vaporises in the hot nip and thus selectively softens the outer fibres of the paper web. Addition of water to the paper web prior to the calendering has no beneficial effect however over high temperature gradient calendering without moisture addition (90). The reason may be that, as the time is too short for the water to be absorbed into the polymers to any substantial extent, the surface fibres are initially no softer than they are prior to moisture addition. The softening within the nip comes in both cases from the increase in temperature and from the vaporised moisture acting as a plasticizer. With more free water present, more energy is required for the vaporisation of this water, and this should lead to lower temperatures in the calendering nip. In terms of softening, similar situations should thus be reached both with and without the addition of free water, when the initial moisture content is around the usual 9%.

The large benefits of hot nip calendering of newsprint may well be due to the fact that a sufficiently high temperature is reached so that the lignin in the fibre is also softened (91). When the lignin solidifies, these fibres will be more firmly confined to the surface of the paper and will also be less susceptible to later moisture changes at lower temperatures, as the lignin softening temperature would thus not be reached. This may be one reason why the linting propensity is greatly reduced by hot temperature calendering (94).

An important mechanism in hot nip calendering, especially of paper of mechanical pulp, may be the vaporisation of water occurring after the calender nip and leading to a rapid lowering of the temperature of the surface layer, figure 24 (91). This rapid decrease in temperature immediately solidifies the lignin and thus increases the stiffness of the previously soft surface fibres or layer, preventing any relaxation and spring back of these compressed fibres. This leads of course to an inherent risk of stress relaxation if these dried-in stresses are released. Some of these effects are noticed in the increased roughness of the base paper after coating of calendered papers (95). In the coating operation, large amounts of water are applied. The stress relaxation occurring due to this water application, increases the surface roughness of the paper although it does not seem to be particularly confined to the surface fibres of the paper (96). The stress release seems rather to affect the whole bulk of the paper, presumably as water penetrates the whole paper structure in the coating of low grammage paper, and thus increases the thickness of the paper (97).

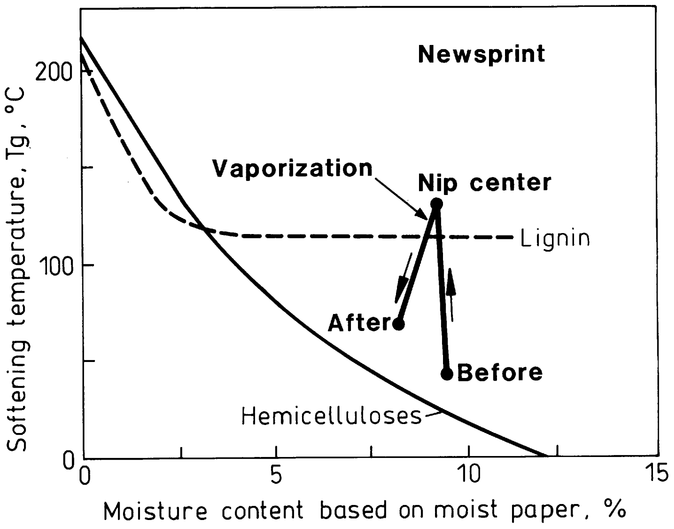

Figure 24 Schematic picture of the temperature and moisture changes on hot calendering of newsprint in relation to the glass transition temperature of lignin and hemicelluloses. Softening and resolidification of the heated surfaces occur when the softening temperature of the lignin is passed (91)

Corrugating

Another operation in which high temperature softening of the wood polymers is utilised is the corrugating process. In the nip of the corrugator at standard speed (100-200m/min), the medium reaches a temperature of 130° to 160°C with 4 to 8% moisture content (98-100) illustrated in figure 25, in which the temperature measured in the middle of a paper corrugated at moderate speed is plotted. To increase the softening, the paper is in most cases presteamed prior to the corrugating nip. As is the case with high temperature calendering, a temperature high enough to soften the

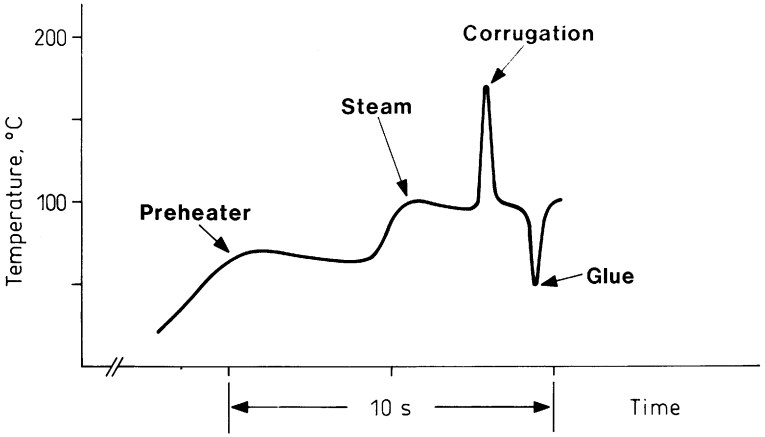

Figure 25 Temperature of a corrugating medium during the fluting operation at a speed of 16m/s with a corrugator surface temperature of 180°C (101)

lignin is reached and the sulphonated lignin of NSSC pulps can begin to flow, a property reached at about 50°C above the softening of a polymer, see figure 26.

The softening achieved in the medium entering the corrugating nip appreciably reduces the elastic modulus of the paper and thus enables it to be moulded into the fluted shape (99). When the paper leaves the nip, moisture vaporises and leads to a sudden decrease in temperature. At this stage, the lignin solidifies and the fluted form is thus retained. The stability of the fluted profile is highly dependent on this freezing-in of the deformed structure which to a high degree is dependent on lignin solidification (101). This may be the reason why NSSC-based corrugating medium paper has a better performance than a medium based on other sources with, in most cases, a lower lignin content (100, 101).

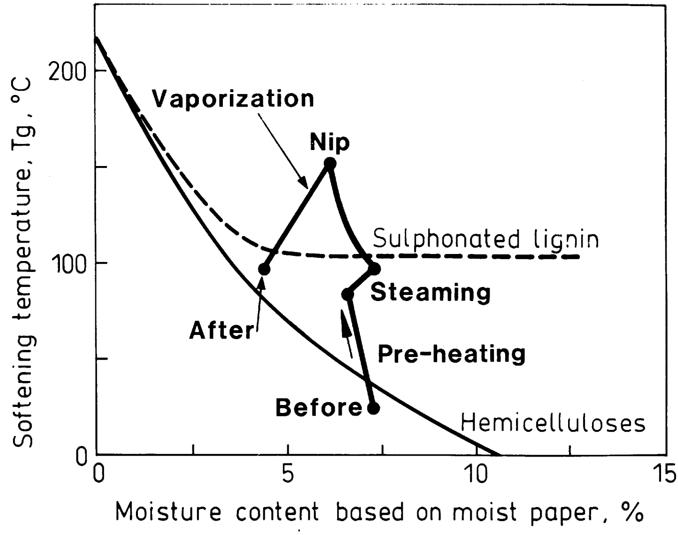

Figure 26 Schematic picture of the temperature and moisture changes in a corrugating medium when it passes through the fluting operation (101)

Press drying

The idea of producing better quality packaging papers from low grade hardwood pulps by press drying has been around for some time, (see 102). The idea is in itself an extension of the hardboard press operation applied to paper with temperatures reaching above 150°C in the paper in the press nip. In both cases, it is the amorphous wood components, the hemicelluloses and especially the lignin, which are softened. By achieving conditions under which these wood polymers can flow, the fibres are made sufficiently flexible for them to be able to conform and bond to each other as a result of the more adhesive nature at this elevated temperature (103). That lignin flows in the press drying operation is particularly evident in the increased wet tensile strength of the product (104). This flow of lignin can to some extent protect the bonding sites from water and thus enhance wet-strength properties. However, at these high temperatures, auto-oxidative cross-linking must also be taken into consideration as a process making the material more water resistant (105). The process is also sensitive to the moisture content of the paper. The lower the moisture content, the higher is the temperature needed to achieve a sufficient bonding (106). It is also noticeable that, for high yield pulps, the creep rate in a cyclic environment is substantially lowered by press drying (107). Thus it seems probable that lignin flow to some extent protects the hydrogen-bonded structure of the carbohydrates from debonding as a result of the moisture movement under sorptive conditions.

Effects in printing and converting operations

Dimensional stability

For printing papers and packaging materials used in high speed packing machines, dimensional stability is of great importance. Of special interest is the relation between the hygroexpansivity of the paper and the dried-in stresses built into the paper during its drying on the paper machine. As indicated earlier, dried-in stresses will to a great extent reduce the hygroexpansivity of the paper, but the uncontrolled release of these dried-in stresses may cause trouble in different processing operations. Depending on the particular operating conditions, different situations may arise. For instance, in xerography, the paper essentially shrinks due to the loss of water and is only affected by the hygroexpansivity at low moisture contents. Release of dried-in stresses is thus unlikely and a high degree of dried-in stresses in the paper may be beneficial giving the paper a high stiffness and a low hygroexpansivity. On the other hand, in processes where water is sorbed, like offset printing, higher overall moisture contents are reached in the paper and the release of dried-in stresses is likely.

It is also evident that the hygroexpansivity measured on a freshly made paper may differ considerably from that of the same paper tested after some month of storage, particularly if the paper has the opportunity, at some stage, to relax at not too low a RH as, for instance, in sheeting operations. The built-in stresses, especially those related to stresses in the hemicellulose, easily relax when stresses are relieved at a higher RH and thus the hygroexpansivity of the sheet may be totally changed.

As hygroexpansivity is a function of the water uptake in the wood polymers, it is obviously not possible to eliminate it without elimination of the water uptake - which requires the total coating of the fibre with a hydrophobic polymer. In some special cases, attempts have been made to minimise dimensional changes by adding a hygroscopic substance like polyethylene glycol to the paper (108) to act as a moisture buffer mediating the moisture changes caused by changes in relative humidity.

The hygroexpansional potential i.e. the hygroexpansivity of the freely dried fibre is, as discussed earlier, intimately tied to the chemical composition of the fibres, the hemicellulose content being the most important factor. However, as the lignin present normally functions as a restraint to expansion as it is at room temperature far below its softening temperature and its moisture uptake is lower, papers of mechanical and chemical pulps have hygroexpansivities of similar magnitude. Of more importance for the hygroexpansivity is the structure and composition of the paper sheet. Due to the lower crystallinity (109), fines material has less hygroexpansional restrictions from the cellulose and thus increases the hygroexpansivity of the paper (110). The presence of fibre deformations, kinks, also increases hygroexpansivity, as also here the restrictions associated with the cellulose fibrils are disturbed in the fibre direction (110).

With respect to relative humidity, the expansion and shrinkage of a freely dried sheet show a hysteresis, but with no irreversible deformation

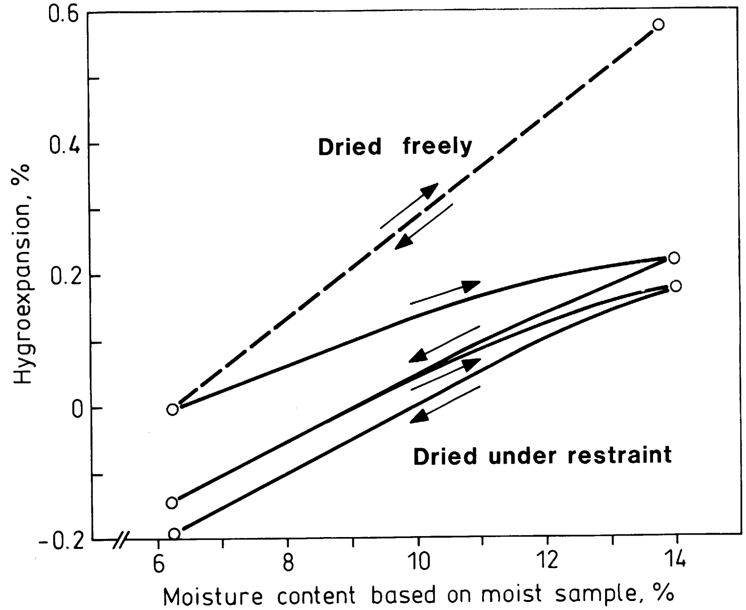

Figure 27 Schematic illustration of the hygroexpansion for freely and restraint dried sheets subjected to several moisture cycles of similar magnitude, (based on data of 111, 112, 114)

depending on the number of moisture cycles (111-113). The hygroexpansion of a freely dried sheet is however identical based on its moisture content, regardless of whether the condition is reached in absorption or in desorption, as with its mechanical properties (111, 113), see figure 27.

For the sheet dried under restraint, dried-in stresses are released above a moisture content of ca 10%, a release which is greater in the first cycles and gradually diminishes as the hygroexpansivity approaches that of the freely dried sheet (111-114). The extent of the release of dried-in stresses, as well as of the hygroexpansion itself, is a complex phenomenon involving the rate of moisture sorption, the viscoelasticity of the paper and how this affects creep and also the effect of relaxation of dried-in stresses (111).

In general terms, it can be stated that the hygroexpansivity of the sheet is governed by the allowable shrinkage and the hygroexpansional potential of the material (110, 111). On this level of refinement, the relation giving hygroexpansion as inversely related to the elastic modulus may be applied, i.e. with increasing modulus the hygroexpansivity decreases (115-117). It has been suggested that the anisotropic ratio of the hygroexpansivity should correlate with that of the elastic modulus ratio in MD and CD (117, 118), but such a relation is a pure coincidence since, in the general case, no such relation exists (110).

Most of the studies relating to effects of hygroexpansivity deal with static or in some cases dynamically changing conditions. In practice, the moisture content may often suddenly change in a stepwise function. The manner in which this affects the hygroexpansion is relatively unknown. The moisture sorption and diffusion through the paper show exceptional behaviour under such conditions (84), and the hygroexpansivity may exhibit similar features.

Curl

Curl problems may be considered as a special case of dimensional instability. In the general case, curl in paper may be caused by irreversible deformations when the paper is bent beyond its elastic limit, by an uneven release of dried-in stresses occurring for instance in the storage of paper rolls, or by an uneven hygroexpansion in the thickness direction of the sheet (116). The latter case is the most common situation not only for board products made up of several layers but also for homogeneous papers, due to an uneven distribution of e.g. fines in the thickness direction, a problem specifically related to Fourdrinier papers. For such paper products, it is common practice to vary the drying conditions on the two sides of the paper in order to obtain a flat product. However, under such circumstances, the release of dried-in stresses may be crucial to the performance of the paper produced. It is essential that such a paper is kept

	Thermal expansivity %/°C	Hygroexpansivity %/%
MD	$3.0 - 7.5 \cdot 10^{-4}$	0.013 - 0.036
CD	$8 - 16 \cdot 10^{-4}$	0.076 - 0.100

Table 2. Comparison of thermal expansivity (118) and hygroexpansivity (120) for paper made of both mechanical and chemical pulps.

at a constant moisture content throughout its service (119). Of special interest may be how the paper performs in subsequent printing and converting operations. It may be important to ensure that the sealed paper roll is opened under conditions such that its moisture content complies with that of the surrounding atmosphere. As the thermal expansivity of paper products is small compared to their hygroexpansion, see table 2, it is not essential to have the paper at the same temperature as that of the surroundings provided the moisture content matches the relative humidity (119). A temperature increase of as much as 100°C leads to an expansion equivalent to the dimensional change of the paper when its moisture content is increased by only 1%.

Surface roughening

The smoothness of the surface is particularly important for printing papers. This paper surface may however be subjected to process conditions, coating and printing where large amounts of water are applied to the surface; water which will have a negative effect on the surface performance. For many papers, the interaction between water and paper leads to an increase in surface roughness as well as an increase in thickness (120,123). There is a noticeable difference between calendered papers which show a large increase in roughness, particularly papers based on mechanical pulps, and uncalendered papers based on mechanical pulp which show no increase or those based on chemical pulp which showed only a marginal increase in roughness (124). In the case of papers of mechanical pulp, this interaction with water also results in a substantial increase in the thickness of the paper (124) which is also evident in the coating of LWC furnishes (97). For chemical pulps no detectable increase in thickness was noticed in contact with water (124).

The large increase in both roughness and thickness in the case of calendered papers based on mechanical pulp is what is expected when stresses introduced by the compaction of the calendering are released by the softening action of the applied water. Apparently the bond strength of chemical pulp fibres is sufficiently high for the thickness to remain constant although some surface fibre debonding or fibre cross section recovery occurs. In the case of mechanical pulps, the stress relaxation phenomenon seems to be distributed throughout the sheet with a close correlation between the thickness increase and the increase in surface roughness. Microscopical observations of the surfaces of papers subjected to wetting and redrying also suggest that the roughening is difficult to associate with fibre debonding (96), which may also suggest a stronger correlation to bulk phenomena. As is evident in the micrographs of figure 28, only a limited debonding is seen when the paper surface is wetted, although there is a 10% increase in paper thickness.

It is interesting to note that the application of high temperature during calendering may to some extent reduce the subsequent surface roughening tendency (89, 124) presumably through the softening and solidification of the lignin which then prevents the release of compaction stresses by water, as the softening temperature of lignin is not reached in subsequent coating and printing operations.

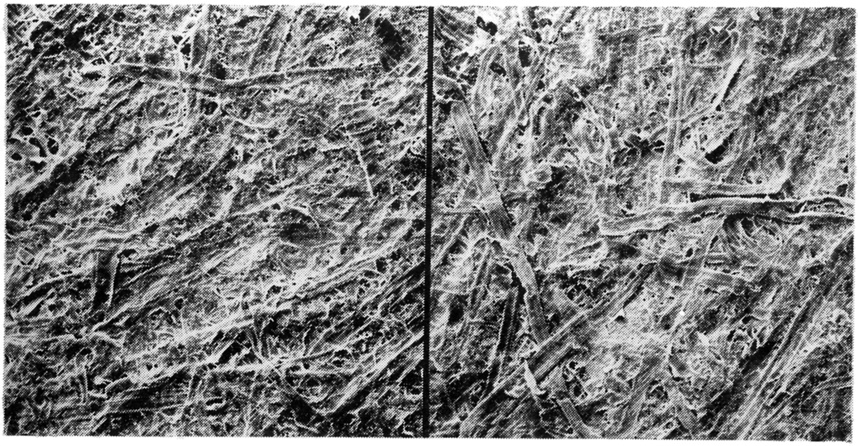

Figure 28 Micrographs of the surface of a TMP paper subjected to a water treatment. Left picture before treatment; right picture after water treatment showing some debonded fibres

Linting and fibre rising

Both linting, i. e. the transfer of fibres to offset printing blankets, and fibre rising are costly problems for printers of newsprint. Linting is a problem of both quality loss and press efficiency loss, while fibre rising leads mainly to a quality deterioration with a lower gloss and higher surface roughness of the paper. Linting may be said to be an extreme form of fibre rising where the total bonding of fibres or debris to the paper surface is lost, and a correlation with the long fibre rising has also been seen (125). A reduction in the long fibre content also reduces the fibre rising. The fibre rising occurring as an effect of water applied to the paper surface is of course linked to the previously discussed phenomenon of surface roughening.

High temperature calendering may bind the surface fibres more tightly, as discussed earlier, and thus reduce the linting problem (94). Calendering at low temperatures has no effect or is even a disadvantage with regard to linting (94). This may be because the fibres are too brittle under these low temperature conditions and are thus disrupted from the surface by the high shear stresses, whereas higher temperatures plasticize the fibres and, possibly by lignin flow, achieve a better bonding between surface and bulk fibres.

THE CHANGING ENVIRONMENT - SUMMARY CONCLUSIONS

The problems discussed in this paper are mostly related to dynamic changes in the atmosphere surrounding the paper. However most of our knowledge of the properties of paper is acquired under equilibrium conditions. In some cases this information may be sufficient, i.e. in determining the final curl in a product exposed to a high constant humidity, but in most cases only a partial stress release will occur during moisture gain as the time for relaxation is too short. The final dimensions and properties of the paper may then depend on its history when it is subjected to a non-systematic changing humidity. The viscoelastic creep occurring as a consequence of moisture-induced stress release has a strong influence on the dimensional stability of products, the long-term creep properties as well as curl. Thus, to obtain a deeper understanding of these problems in the future, much more basic research is needed on properties under dynamic situations; studies on the dynamics of moisture sorption, studies of hygroexpansivity under a changing environment and further studies into the mechanisms of mechano-sorptive creep.

The fact that the wood fibre is a multicomponent material with components that soften at different moisture contents and different temperatures makes the development of internal stresses in the material unavoidable. The resulting effects on properties have been utilised in for example high temperature calendering and corrugating. New knowledge about how to control these stresses may eventually make possible further improvements in properties.

The ionic nature of the paper, i.e. of its wood polymer constituents, also means that the material is highly influenced by the nature of the counterions in the system. This fact has so far been utilised mostly in special sanitary products. Further knowledge concerning the ionic performance of cellulosic materials may make it possible to alter their properties and to make use of them in other products in a beneficial way.

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Transcription of Discussion

RESPONSE OF PAPER PROPERTIES TO CHANGES IN THE SURROUNDING ENVIRONMENT

L Salmén (Review Paper)

Dr W Hewertson, CSIRO, Australia

You made a very important point that was mentioned yesterday regarding defects and I think that this was emphasised in your paper. With the pressure to reduce the use of chlorine and chlorine dioxide in bleaching, manufacturers are now moving to ozone bleaching and extended delignification. Have you done any work on the effect of these two pieces of technology on both the fibre defects and the modulus of the paper zone A?

L Salmén

We haven't done any work on this subject but its likely that both the chemical structure of the components would be affected as well as the distribution of the polymers in the material and that will affect the development of defects and in the end affect properties.

Dr D Priest, UMIST, UK

You talk about the glass transition temperatures as high as 230º I was interested in the experimental arrangements and how it relates to thermal degradation of the cellulose which we often believe starts at temperatures below that.

L Salmén

Yes, this is of course a severe condition for the material so these experiments were done at very short testing times at higher temperatures where the effects of thermal degradation were possible to avoid (see ref 46 p 422).

I Kartavaara, Enso Gutzeit Oy, Finland

Most text book treatises on water absorption give a lot of importance to capillary condensation claiming that capillary condensation begins at somewhere maybe 60% RH. You did not mention capillary condensation at all. Can you share with us your views of the importance and validity of capillary condensation?

L Salmén

Well, for the materials we have tested to 95% RH we may not detect any free water or freezing water as determined by DSC, so then it becomes rather semantic; if one talks about pores and condensation in them they must then be so small that this will occur on the molecular level.

Dr R Shet, Kimberly Clark Corp, USA

My question is regarding the position of the softening point in a composite. You mentioned that this is determined by the most abundant component. Is it based on the weight or the number of the molecules, as an example you may have only 2% of the hemicellulose but on a number basis it might be much larger.

L Salmén

I am not quite sure if I grasped your question right but in a homogeneous blend the position of the transition will be related to the volume percentage of the material present in the blend.

Dr L Wagberg, SCA Research, Sweden

I would like to ask you about the non freezing water, which is also found in, for example super absorbent polymers. In your explanation, to the occurrence of non-freezing water, you mentioned the same mechanism, as for general bonding between water and hydroxyls on celluloses, just different degrees of hydrogen bonding . Is that really the true molecular interpretation. Do you have any other way of explaining this non freezing water?

L Salmén

What we have seen is that there is a very close correlation between the number of hydroxyl groups and the water absorbed and this relates also to other polymers containing hydroxyl groups why I think the explanation is very plausible.

L Wagberg

In my opinion you have to introduce the dramatically increased osmotic pressure in the polymer gel when the number of carboxyl groups is increased. I don't know but perhaps Tony Scallan can give you a hint on the level of the osmotic pressure and the influence this might have on the occurrence of non-freezing water.

Dr A M Scallan, PAPRICAN, Canada

The alternative explanation for the increase in water content due to acidic groups is that their counter ions create an osmotic pressure which draws more water into the fibre wall. This is different to your explanation which was just that there were more water molecules hydrating the acidic groups.

L Salmén

Essentially it is a similar explanation I would say its the acidic groups and its counter ion that controls the moisture content. The type of counter ion will highly affect the level of moisture sorption and maybe you can both interpret this as an hydration shell around the ion and an effect on the osmotic pressure. This will be relevant with the material in water, but it may be difficult to interpret an osmotic pressure with the material in air.

A Scallan

But your interpretation of a hydration shell is not susceptible to quantitative deductions. For example, you showed that a pulp in the sodium form was more hydrated than the calcium form. In terms of the osmotic theory, this extra swelling is because there are twice as many counter ions when you are in the sodium form than when you are in the calcium form and the swelling pressure is proportionally increased.

L Salmén

This effect could be accounted for if you as you say take account of both the number of counter ions and their hydration shell.

L Wagberg

The effect of hydrogen bonding and osmotic pressure should not be treated as similar. Osmotic pressure relates to the entropy of the gel system whereas the hydrogen bonding relates to the enthalpy.

Dr A F Nissan, Westvaco Corp, USA

I have had a problem for over 20 years that's been bothering me. I hope Lennart Salmén will be resolve it for me so that I can sleep easily. You have shown that if you plot the modulus versus moisture content it goes slowly at first and then steeply. As you know very well if you plot that on a logarithmic scale you get a straight line for the steep form for all sorts of papers. You have interpreted the slope of that paper as being influenced by the amorphous portion of the cellulose. Therefore if I had two pieces of paper and they showed me two lines I would deduce from that that one has a more amorphous ratio than the other, a straight forward explanation. My problem is this if you take one piece of paper, and measure the modulus on an Instron with moisture you get a very nice accurate straight line of the logarithms of 'E' versus the moisture content but if you take the same piece of paper and measure the modulus dynamically as Dr Baum and Dr Habegar do you get a nice straight line over a very wide range up to the fibre saturation point but the two straight lines are not coincident. Do we have two fractions for the amorphous ratio? One being detected by the dynamic and the other by the static or what does happen that we have two very distinct, very accurate, very precise repeatable straight lines over a very wide range. I should also tell you that I have no explanation for this on the hydrogen bond theory - that's why it bothers me.

L Salmén

I think this relates to Dr Baum's presentation yesterday**. He pointed out the difference in frequency between the static measurements on the Instron and the dynamic ultrasonic measurements which are done at much higher frequencies where other transitions in the material, the β and γ transitions, are involved in the mechanical properties and not the α transition, the glass transition that affects properties at lower frequencies. Your statement merely points to the importance of this fact that these secondary transitions probably are influencing the ultrasonic measurements.

**** NB: THIS STATEMENT RELATES TO A FIGURE SHOWN IN DR BAUM'S PRESENTATION WHICH DOES NOT APPEAR IN VOLUME 1 - THE FIGURE IS INCLUDED IN VOLUME 3 HOWEVER. (Editor's note)**